VOL. IV. 1903

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

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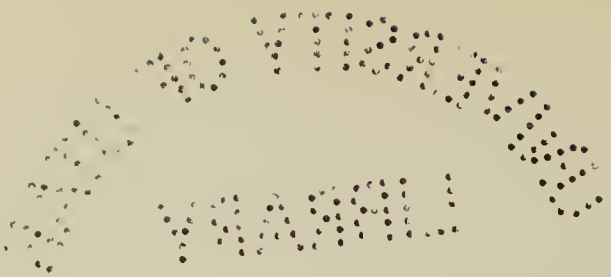
VOLUME IV

FOURTH GENERAL MEETING

NIAGARA FALLS, N. Y., SEPTEMBER 17, 18, 19, 1903

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY
929 CHESTNUT ST., PHILADELPHIA, PA.
1903



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One copy of the *Transactions* is supplied gratis to each member of the Society.

Price of Vol. IV., bound in cloth, $3.00, net. To Colleges, Libraries, Societies and Journals, bound in Cloth, $2.00, net.

A Directory of Members may be obtained from the Secretary on application.

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VOLUME IV. 1903.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

MINUTES OF THE FOURTH GENERAL MEETING OF THE SOCIETY, HELD AT NIAGARA FALLS, N. Y., SEPTEMBER 17-19, 1903.

(Number of members registered, 86; guests, 53; total, 139.)

SESSION OF SEPTEMBER 17TH.

The general meeting was called to order at 10 A. M., in the Assembly Hall of the Cataract House, President Richards being in the chair, and C. J. Reed present as secretary. The chairman addressed the meeting, as follows:

"The present year has been a very successful one in the growth of our Society. The number of members has very nearly reached the six hundred mark, and it will be gratifying to you to know that there were 45 applicants elected this month to membership. The Treasurer of the Society has also reported the finances in a flourishing condition. With all our obligations met at the present time, there is a surplus of about $2,000 assets, which, of course, is mortgaged to pay for the forthcoming volume—Volume IV—but which will be ample to pay for that and for the expenses of the Society for the rest of the current year. The Executive Committee of your Society has quite recently arranged with the Faraday Society, of England, for an exchange of Transactions,

the action has been ratified by the Board of Directors, and will go into effect as soon as our foreign friends can furnish their monthly journal to us. It amounts to each member of our Society receiving monthly the *Electrochemist and Metallurgist,* which is the organ of the Faraday Society; and which will be mailed separately to each member directly from England; while in return we send to each member of the Faraday Society a copy of our Transactions. This will be done without any increase in the membership dues; and we have calculated that the extra cost of publishing these volumes can be easily met by our treasury in its present condition. If possible, we will try to get for our members the July and August numbers of the *Electrochemist and Metallurgist,* but as the arrangement was not completed until those numbers were printed, it is doubtful if enough were printed to supply all our members. The Board of Directors also to-day directed our Executive Committee to draw up regulations establishing local sections, the matter being brought before it in the shape of a request from our members at the University of Wisconsin, at Madison, to establish a local section there. The board has taken a broad view of this matter, and regulations will be drawn up governing the establishment of local sections wherever they are requested; this is probably the starting point of a very wide expansion in the usefulness of our Society. It is intended that these local sections shall hold monthly meetings, if possible, for the discussion of electrochemical subjects, and that the best of the papers there presented will be brought before the general meetings of the Society. Those are the main topics of general interest which have been acted on since your last meeting; and I am sure that, although we have but a modest attendance, yet the enthusiasm of this meeting and the interest and the benefit which will be derived by those participating in it, will not be any less than in any meeting which we have had heretofore." (Applause).

The following papers were then read and discussed, as printed in full in the Transactions:

"Some Theoretical Considerations of Resistance Furnaces," by Mr. F. A. J. Fitz Gerald.

"Advances in the "Electrometallurgy of Iron Production," by Mr. Marcus Ruthenberg.

"A Practical Utilization of the Passive State of Iron," by Prof. C. F. Burgess.

SESSION OF SEPTEMBER 18TH.

The meeting opened at 9.30 A. M., in the same hall, with the same officials present.

The following papers were read and discussed, as printed in full in the Transactions:

"An Experiment on the Electrolytic Determination of the Basicity of Acids," by Mr. I. J. Moltkehansen.

"The Electrometallurgy of Gold," by Dr. W. H. Walker.

"Electrolytic Copper Refining," by Dr. W. D. Bancroft.

(Discussions on this paper, communicated by Mr. Lawrence Addicks, Mr. B. Magnus, and Prof. T. R. Rosebrugh, were read by the chairman.)

"The Efficiency of the Nickel-Plating Tank," by Prof. O. W. Brown, read by Mr. W. McA. Johnson.

"A New Type of Electrolytic Cell," by Mr. Pedro G. Salom.

"Electrolysis of Sodium Hydroxide by an Alternating Current," by Dr. Carl Hambuechen, read by Prof. C. F. Burgess.

"The Electrolysis of Water" (Paper II), by Dr. J. W. Richards and W. S. Landis, read by Dr. Richards; Prof. W. D. Bancroft occupying the chair.

SESSION OF SEPTEMBER 19TH.

The meeting was called to order at 9.30 A. M., in the same hall, and with the same officers as before.

The following papers were read and discussed, as printed in full in the Transactions:

"On the Supposed Electrolysis of Water Vapor," by Mr. F. Austin Lidbury.

"Note on the Use of Metallic Diaphragms," by Dr. E. A. Byrnes, read by Mr. C. P. Townsend.

The remaining papers dealt with the Theory of Electrolytic Dissociation, in its various aspects, and were read in the following order:

"The Theoretical Properties of Free Ions in Solutions," by Dr. E. F. Roeber.

"Discussion of the Theory of Electrolytic Dissociation," opened by Prof. W. D. Bancroft.

"The Thermochemistry of the Dissociation Theory," by Dr. J. W. Richards.

"Berthelot's Law Relative to the Electromotive Force of Cells Based on the Reciprocal Action of Saline Solutions and Soluble Electrolytes," by Mr. C. J. Reed (read by title).

The discussion was participated in also by Prof. H. S. Carhart, Prof. H. M. Goodwin, Dr. W. L. Miller, Dr. Rudolph Gahl, Mr. A. H. Cowles, Mr. F. A. Lidbury, and others.

The reading of papers and discussions being closed, on motion of Mr. Carl Hering, the thanks of the Society were extended to the National Battery Co., of Buffalo, the Niagara Research Laboratories, the Niagara Power Co., and the Local Committee of the Society, for their co-operation and efforts in insuring the pleasure of the visiting members and guests of the Society. The motion being carried, the meeting adjourned at 12.30 P. M.

C. J. Reed,
Secretary.

PROCEEDINGS OF DIRECTORS.

ABSTRACTS FROM THE MINUTES OF THE MEETINGS OF DIRECTORS AND THE EXECUTIVE COMMITTEE, HELD MAY 9TH TO SEPTEMBER 17TH, 1903.

The Board of Directors appointed the following members as its

EXECUTIVE COMMITTEE.

Dr. J. W. Richards, president; C. J. Reed, secretary; S. Reber, Carl Hering, S. P. Sadtler, P. G. Salom.

The following members of standing committees appointed by the president, were confirmed:

PUBLICATION COMMITTEE.

Dr. J. W. Richards, president; C. J. Reed, secretary; C. Hering, P. G. Salom, W. D. Weaver.

COMMITTEE ON PAPERS.

Dr. J. W. Richards, president; C. J. Reed, secretary; Dr. C. A. Doremus, Dr. E. F. Roeber, Prof. C. F. Burgess, F. J. Tone, D. H. Browne, Dr. H. S. Carhart, Dr. H. T. Barnes, C. P. Townsend.

MEMBERSHIP COMMITTEE.

Dr. H. T. Barnes, Dr. E. A. Byrnes, Dr. H. S. Carhart, A. H. Cowles, Dr. V. Engelhardt, J. S. Fitzmaurice, Prof. P. A. Guye, R. S. Hutton, A. von Isakovics, Dr. L. A. Parsons, Henry Noel Potter, F. J. Tone, Dr. H. L. Wagner, Dr. W. R. Whitney, F. M. Zeller.

The committee appointed at the New York meeting to consider the advisability of co-operating with foreign electrochemical societies, reported favorably to the Executive Committee, and a free exchange of transactions with the Faraday Society was effected.

An invitation from the Chief of the Electrical Department of the St. Louis World's Fair, to hold a general meeting of the Society at St. Louis during the week of September 12th to 17th, 1904, was accepted, the exact date of the meeting to be arranged later.

President Richards was authorized as a member of the Committee on Arrangements for the International Congress of Electricity, to be held in St. Louis in 1904, and as representative of the American Electrochemical Society, to negotiate with said committee of the International Congress, and to arrange for publication of the papers to be read at the electrochemical section of the congress in the Transactions of the Society as part of our proceedings, and he was empowered to conclude such an arrangement.

At the meeting of directors, held August 7th, the President, Secretary and Treasurer were appointed a Finance Committee to examine all bills against the Society and to make recommendations to the Board of Directors as to their approval.

It was ordered that in future all bills after being paid by the Treasurer are to be returned to the Secretary, who is to keep them on file and render to the Treasurer a receipt therefor.

A proposition of Ware Bros. Company, of Philadelphia, for publishing Vol. IV, of Transactions, was accepted.

It was ordered that in future all proof of publications is to be submitted to each member of the Publication Committee before going to press.

At the meeting of September 17th, the Treasurer presented the following statement of the financial condition of the Society on the 14th of September:

RECEIPTS.

Balance, January 1, 1903	$879.49	
From publications	208.95	
" Expense	8.60	
" Advertising	49.70	
" A. B. Frenzel Prize	250.00	
" Members, in fees and dues	3,159.00	
	$4,555.74	$4,555.74

EXPENDITURES.

For Expenses	$946.73
" Publication	959.97
" Office furniture	53.00
Balance in Fourth Street National Bank	2,596.04
	$4,555.74

There is due to the Society from Members.

From 48 members, at $ 5.00	$240.00
" 49 members, at 10.00	490.00
	$730.00

MEMBERS ELECTED JUNE-OCTOBER, 1903.

June 13th.

F. E. Drake, New York; I. J. Moltkehansen, Perth Amboy, N. J.; F. T. Snyder, Oak Park, Ill.; Dr. H. Reisenegger, Augsburg, Germany; Robert Spice, New York; Dr. Leo Baekeland, Yonkers-on-Hudson, N. Y.; H. Wigglesworth, New York; H. J. Lucke, Washington, D. C.; S. W. Traylor, New York; Dr. Paul Askenasy, Nurnberg, Germany; Dr. Rudolf Gahl, Philadelphia, Pa.; H. B. Cornwall, Princeton, N. J.; B. F. Thomas, Chattanooga, Tenn.; H. A. Jackson, New York; C. E. Speirs, New York.

August 7th.

George M. McKee, Hinckley, N. Y.; Wm. J. Hammer, New York; James A. MacDonald, New York; Max M. Haff, Ottawa, Canada; F. A. Lidbury, Niagara Falls, N. Y.

September 4th.

M. L. Davies, Bay City, Mich.; Charles M. Perry, Pawtucket, R. I.; P. E. True, Elizabeth, N. J.; T. B. Stillman, Hoboken,

N. J.; L. M. Dennis, Ithaca, N. Y.; Alan A. Claflin, Littleton, Mass.; Heyward Scudder, Boston, Mass.; J. H. Beal, Scio, Ohio; Ernst Fahrig, Philadelphia, Pa.; J. G. White, New York; Anthony Gref, New York; C. C. Curtis, Sandusky, Ohio; W. S. Howell, New York; W. R. C. Corson, Hartford, Conn.; Dr. Louis Duncan, Boston, Mass.; Ervin Dryer, Chicago, Ill.; C. D. Brown, Windsor, Conn.; J. A. Wotton, Atlanta, Ga.; J. L. Merrill, Pittsburg, Pa.; M. W. Hanks, Pittsburg, Pa.; J. M. Kent, Kansas City, Mo.; E. A. Sjostedt, Sault Ste. Marie, Ont., Canada; H. N. McCoy, Chicago, Ill.; E. H. Clapp, Boston, Mass.; Dr. George P. Scholl, Philadelphia, Pa.; Dr. Franz Meyer, New York; Alonzo C. Bell, New York; Stephen Gardner, Chicago, Ill.; E. O. Schweitzer, Chicago, Ill.; H. B. Smith, Worcester, Mass.; G. C. Rowe, Havana, Cuba; H. Wingate, Forest Hill, London, England; W. T. Earl, Niagara Falls, N. Y.; G. W. Bauer, San Francisco, Cal.; S. Tada, New York; R. T. Conger, Pittsfield, Mass.; H. S. Wilson, Pueblo, Mexico; E. B. LeMare, Manchester, England.

September 17th.

W. H. Davis, Bear, Idaho; Dr. Michael Sack, Lockport, N. Y.; J. F. McElroy, Albany, N. Y; William Valentine, Lansingburgh, N. Y.; Elihu Thomson, Swampscott, Mass.; H. H. Seabrook, Washington, D. C.; E. E. Armstrong, Niagara Falls, N. Y.

October 9th.

Paul J. Kruesi, Chattanooga, Tenn.; Sherard Cowper-Coles, London, England; W. A. Johnston, Prince Bay, N. Y.; I. A. H. Glenck, Riga, Russia; R. N. Kofoid, Niagara Falls, N. Y.; J. F. Merrill, Salt Lake City, Utah; C. E. Finney, New York; R. H. Aiken, Sault Ste. Marie, Ont., Canada; Joseph Bijur, New York; H. T. Darlington, Philadelphia, Pa.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, September 17, 1903, President Richards in the Chair.

NOTE ON SOME THEORETICAL CONSIDERATIONS IN THE CONSTRUCTION OF RESISTANCE FURNACES.

By Francis A. J. Fitz Gerald.

Electric furnaces are usually divided into two great classes—arc furnaces and resistance furnaces. The latter class may be divided into two sub-classes—furnaces in which the current passes through the whole charge and those in which the current passes along a definite path or paths, thus localizing the heat. It is to the latter type that this paper will chiefly apply, although some reference may be made to the former. An apology for this paper seems necessary, since to those who have done much work of this kind the considerations presented will appear to be obvious and elementary. But it is believed that those who have had little experience in the construction of furnaces may find here some suggestions that will be of assistance in furnace design.

Of the various electric furnaces that have been developed, those due to Mr. E. G. Acheson present unusual interest, because they cover a considerable range of temperature and involve certain conditions as to accurate temperature regulation.

Graphite Furnace.—In this furnace the highest temperature attainable is desired. The carbonaceous material, anthracite coal, coke, etc., is placed in a trough-like furnace, and through the center of the charge is a series of carbon rods connecting the furnace terminals. Anthracite coal, the raw material usually employed, is practically a non-conductor of electricity, and at first the current passes through the core of carbon rods. The heat generated in the core converts the surrounding coal into graphite, which then becomes a conductor and heats another layer of coal, and so on till the process is complete. This furnace belongs to both sub-classes of the resistance type.

Graphite Electrode Furnace.—The furnace belongs to the first sub-class, but is peculiar in that the heat is mainly generated out-

side the articles under treatment. In the most general case the electrodes to be converted into graphite are arranged in piles, and the spaces between the latter filled with granular carbon. Since the resistivity of the granular carbon mass is much greater than that of the electrodes, most of the heat energy will be developed in the former. The advantage of this type of furnace is that it permits of treating a large mass of low-resistance material without using currents of excessive amperage.

Carborundum Furnace.—Carborundum is a substance that is decomposed at the temperature of the graphite furnace, hence in its manufacture careful temperature regulation is necessary. The charge, consisting of sand and coke, in the form of powder, is put in the box-like furnace, and through its center passes a conducting core, which may consist of carbon in a granular form, or of carbon rods, connecting the terminals of the furnace. The current is confined to the core, raising it to a high temperature, and the heat generated is conducted into the surrounding mixture, converting it into carborundum. If the temperature of the furnace is too high, the carborundum is decomposed and the silicon vaporized.

Furnace for Moderately High Temperatures.—This is the latest of Acheson's patents, and is of great interest. In the outer zone of the carborundum furnace, just outside the crystalline silicon carbide, is a thin layer of an amorphous substance, known as "white stuff." It is an intermediate product in the formation of carborundum, and the temperatures between which it is formed and decomposed apparently lie near one another. For this reason its manufacture, or that of like compounds, involves serious difficulties, and it was to overcome these that Acheson invented this furnace. The furnace is of the same general form as that used in the manufacture of carborundum, but it contains several cores, which are "definitely spaced with relation to each other at distances largely determined by the heat conductivity of the charge, the duration of the operation and the superior and inferior temperature limits of the operation."[1]

[1] U. S. Patent 723,631, March 24, 1903.

In all of the furnaces described above there is one common characteristic—the electrical resistance is a variable quantity, and after any furnace is started there are no means of adjusting internal conditions so as to effect regulation in this respect. In general, the resistance of these furnaces is high at the beginning of a run and low at the end; therefore, means of varying the voltage at the furnace terminals must be used. If the furnace resistance at the beginning of a run is R, at the end of the run r, the maximum voltage attainable E, the minimum voltage e and the maximum watts W, then the following equations must hold:

$$R \leqq \frac{E^2}{W} \qquad (1)$$

$$r \geqq \frac{e^2}{W} \qquad (2)$$

The application of these equations to the various furnaces considered is obvious. The resistance of the furnace may be varied by altering the dimensions of the core or that part of the furnace which acts as an electrical conductor. Later we shall see that there are limits to the variations that can be made in this respect on account of other considerations; but the resistivity of a mass of carbon granules varies with the size of the latter, and further variation may be obtained by the judicious choice of different forms of carbon, which themselves have different resistivities. By taking advantage of this, any desirable variations in the resistance of the furnace may be obtained. The case of the electrode furnace is a special one, the adjusting of the resistance being obtained, to a certain extent, by the spacing between the piles of electrodes.

If a cylinder is kept at a constant temperature, θ_1, and is surrounded by a heat-conducting material, then the quantity of heat, Q, passing from the cylinder into the surrounding material per second is given by the equation

$$Q = 2\pi\rho_1 LK(\theta_1 - \theta_2)$$

where ρ_1 is the radius of the cylinder, L its length, θ_2 the tem-

perature of the surface of the material in contact with the cylinder and K is a constant. Then

$$\theta_1 - \theta_2 = \frac{Q}{2\pi\rho_1 LK}$$

Now, if θ_2 is a constant and a certain quantity of heat, Q, is developed in the cylinder, then, in order that θ_1 may be kept constant, $\rho_1 L$ must have a definite value. If the cylinder is a conductor heated by a current of W watts, then

$$\frac{W}{\rho_1 L} = \text{constant} \qquad (3)$$

If the material surrounding the cylinder is in the form of a second cylinder, co-axial with the first, then if ρ_2 is the radius of the second cylinder, K^1 the heat conductivity of the material of which it is composed and θ_3 the temperature of its outer surface, it may be shown[1] that

$$Q = \frac{2\pi LK^1 (\theta_2 - \theta_3)}{\log \frac{\rho_2}{\rho_1}} \qquad (4)$$

Next let it be assumed that the outer cylinder is surrounded by a material having a heat conductivity k, and that a certain amount of heat is absorbed at the outer surface of the cylinder, then apply-

[1] In this case the isothermal surfaces about the cylinder are a series of co-axial cylinders, and the lines of flow of the heat form tubes of flow having the shape of wedges, with their edges lying parallel to the axis of the cylinder. Planes parallel to the axis of the cylinder will cut off from the wedges rectangles of equal length, having widths proportional to their distances from the axis; therefore, the heat passing through unit area of the rectangles will be inversely proportional to their distances from the axis. The equation of the flow of heat is

$$= \frac{d\theta}{d\rho} = \frac{a}{\rho}$$

where a is a constant; hence

$$\theta = -a \log \rho + b$$

then at the inner and outer surfaces of the second cylinder

$$\theta_2 = -a \log \rho_1 + b$$
$$\theta_3 = -a \log \rho_2 + b$$

so that

$$a = \frac{\theta_2 - \theta_3}{\log \frac{\rho_2}{\rho_1}}$$

The quantity of heat passing through the cylinder per second is

$$Q = -2\pi\rho LK^1 \frac{d\theta}{d\rho}$$
$$= 2\pi LK^1 a$$
$$= \frac{2\pi LK^1 (\theta_2 - \theta_3)}{\log \frac{\rho_2}{\rho_1}}$$

ing equation (4) to an isothermal surface, outside the cylinder, having a temperature θ_4 and a radius ρ_3, the quantity of heat passing from the cylinder to the isothermal surface per second is

$$q = \frac{2\pi L k\ (\theta_3 - \theta_4)}{\log \frac{\rho_3}{\rho_2}}$$

or if $\rho_3 - \rho_2 = t$, and t is very small,

$$q = 2\pi L k\ (\theta_3 - \theta_4)\ \frac{\rho_2}{t} \qquad (5)$$

In using the results obtained from these calculations, it must be remembered that they only apply approximately, representing as they do hypothetical conditions and involving various assumptions that are not rigorously correct. Keeping this in mind, the various furnaces described may be considered.

Graphite Furnace.—The furnace having been designed so as to fulfill the conditions of equations (1) and (2), it remains only to apply equation (5). The heat developed in the furnace is used in various ways—in raising the temperature of the furnace charge; in effecting chemical changes; in vaporizing substances other than carbon; in supplying heat lost by radiation. With the exception of the last, all these items represent useful work. The last item is represented in equation (5), and, leaving all other losses out of consideration, the efficiency of the furnace is given by the equation

$$\text{Efficiency} = \frac{Q - q}{Q} \qquad (6)$$

In order, therefore, to make q as small as possible, k and $\theta_3 - \theta_4$ should be small. The important point to observe, however, is that a furnace may be made indefinitely large, so far as equations (1) and (2) are concerned, but equation (5) sets a limit, since q varies directly as the product of L and ρ_2.

Graphite Electrode Furnace.—The equations apply to this furnace in a similar way to the previous one.

Carborundum Furnace.—Applying equation (4): ρ_1 is the

radius of the core, or the inside of the carborundum cylinder, θ_2 the temperature of that surface, ρ_2 the radius and θ_3 the temperature of the outside surface of the carborundum cylinder, while K^1 is the conductivity of the crystalline mass. The equation may be written

$$\log \frac{\rho_2}{\rho_1} = \frac{2\pi L K^1 (\theta_2 - \theta_3)}{Q}$$

In order, therefore, to make the maximum amount of carborundum around the core, K^1 must be as great as possible. This can be best accomplished by having the mixture surrounding the core of high density, for then the crystal mass formed will also be dense. $\theta_2 - \theta_3$ should also be as large as possible, but θ_3 is a constant, the temperature just below that of the formation of carborundum; therefore, θ_2 should be as large as possible. But θ_2 cannot be indefinitely increased, for above a certain temperature carborundum is decomposed. Hence equation (3) applies here, for the value of $\rho_1 L$ must be such that the core temperature shall be just less than that which will cause the decomposition of carborundum.

Finally, in considering the outside of the carborundum cylinder, equation (5) is used. As before, k and $\theta_3 - \theta_4$ must be kept as small as possible. Nothing can be done to diminish k, as the material outside the carborundum must of necessity consist of the unchanged mixture of sand and coke. Fortunately, the mixture has a very low heat conductivity. $\theta_3 - \theta_4$, however, may be kept small by leaving a good thickness of unchanged mixture outside the carborundum. It will be observed that since the value of ρ^2 increases with the length of the run, a point will finally be reached where q is equal to Q in equation (6); or, in other words, the efficiency of the furnace continually diminishes as the length of the run increases, and a point is at length reached where no more carborundum is made. In order to work efficiently, the run must be stopped long before that point is reached.

Furnace for Moderately High Temperatures.—Here the conditions are similar to those in the carborundum furnace, but more complicated, as there is a multiplicity of cores. However, the theoretical considerations that have been discussed will still prove useful in giving a general idea of the furnace design.

In no case that has been considered can the various fundamental equations be rigorously applied, for, as has been pointed out already, these involve numerous assumptions that do not represent the actual conditions, and take no account of certain conditions that are invariably present. Nevertheless, it will be found that keeping the theoretical considerations in view is a great help in the building of furnaces, and prevents waste of time in experimenting with designs that cannot possibly be satisfactory.

DISCUSSION.

PROF. C. F. BURGESS: I should like to inquire whether the power factor of the furnaces, such as have been described, approach unity; in other words, whether the current and pressure readings will enable an accurate calculation of the power consumption to be made.

MR. F. A. J. FITZ GERALD: I do not know what the power factor of carborundum and graphite furnaces is. With the heavy currents used there is serious self-induction in the circuit, and for that reason the bus bars are interlaced in the best practice. On some actual measurements that were made at the Carborundum Works before the bus bars were interlaced, the power factor was found to be very low.

MR. A. H. COWLES: He says: "Just outside of the carborundum occurs the layer known as 'white stuff.'" In 1885, I performed an experiment on carbon and sand and got carborundum; and in that zone between unreduced silicon and the carborundum I noted a material that was totally different from that which was completely reduced, and different from sand, and I could not account for it, unless it was a case of silica being partly reduced, forming a suboxide of silicon that was unknown in chemistry at that time. I took some of the product and gave it to a professor of chemistry to be examined, and he did a large amount of work on it. The result of the work was that it was a case of silicon acting as a dyad instead of a tetrad: a suboxide of silicon, it may be. Has Mr. Fitz Gerald ever identified a suboxide of silicon, SiO? If so, it would be confirmatory of the

work of Dr. Mabery in 1885, and it would be the only case in chemistry where silicon is acting as a dyad instead of a tetrad.

Mr. Fitz Gerald: I have made several analyses of the substance known as "white stuff," and have never found any evidence of the existence of suboxide of silicon. In white stuff there seem to be certain compounds containing carbon, silicon and oxygen, possibly of a similar nature to those described by Colson and Schutzenberger. Schutzenberger also produced a substance of which the description corresponded to that of white stuff, and showed that it had the formula SiC.

Mr. Carl Hering: I have been interested in some of the formulas which Mr. Fitz Gerald gave, as I had occasion to use similar formulas some time ago in making calculations concerning electric furnaces. I regret, however, that he did not give the actual units in terms of which those formulas are correct quantitatively; they would then be much more serviceable. To use them one should know whether the lengths are in inches, in what scale the temperatures are given, and approximately what the constants are. As they stand, the formulas merely give relative results; with known units they would give actual, quantitative results. I had considerable difficulty in finding out what the units were in some similar formulas, before I could use them.

Mr. Fitz Gerald: These equations have not been applied to actual furnaces, except in an approximate way. The object of working out these equations was to give a general idea of the theory of furnace design. As I pointed out in the paper, there are a great many assumptions made that are not rigorously correct. For example it is assumed that the value of K is constant, which certainly is not the case. In the carborundum cylinder the value of K is probably much greater next the core of the furnace than in the outer parts. Again, no account is taken of the radiation losses from the ends of the furnace, so I doubt if the equations could be applied to a concrete case without modification.

Mr. Cowles: Does not the current also pass through the carborundum that forms around the core? Is not that your experience?

Mr. Fitz Gerald: I do not think any current passes through the carborundum, but it is confined wholly to the core, for carborundum is a non-conductor compared to carbon.

MR. COWLES: You mentioned in your paper that the resistance of your furnace falls very rapidly towards the end of the run. The fact is, it falls about four-fold: the resistance is about four-fold less; whereas, carbon, heated up to the temperature at which it would be in the furnace, should fall not much over two-fold—thus indicating that the current is not only being carried by the carbon, but also by the carborundum that forms around it. To prove that, I once had a furnace made, and after the run had been going and the furnace was fully heated and a large amount of carborundum was formed, I had the furnace so arranged that the bottom could be dropped out of the furnace and a granular core removed. The readings of the current were taken before the removing and after the removing of that granular core; and the current fell off about one-fourth as a result of dropping the core out of the furnace. After it thus dropped out, the only thing that was carrying the current was the charge that was around the core. Thus it was definitely and conclusively proven that the carborundum in the furnace is carrying the current as well as the core, and I have also placed between two electrodes pieces of carborundum and the currents were so large that I could heat them to a red heat, thus showing that heated carborundum is also a conductor as well as the carbon of the core.

MR. FITZ GERALD: I never saw an experiment like that described by Mr. Cowles performed. As regards the lowering of the resistance of the core, it must be remembered that at the beginning this core consists of granular coke, and is eventually converted into graphite, of which the resistance is about one-fourth that of the original carbon. As to carborundum conducting a current, it is well known that a great many substances described as pyro-electrolytes will carry a certain amount of current when very hot, but the point I wish to make is that, hot or cold, carborundum is a non-conductor compared with carbon.

MR. COWLES: My experiment of placing it between two electrodes gave me the impression that it conducted about as well as carbon in the same condition. You take a piece of carborundum in your hand and touch a wire where you can pass a current through your body. You get a very decided shock. That it is a decided conductor anyone can determine by simply taking a shock through a piece of carborundum.

PROF. BURGESS: Some measurements which were made in my laboratory showed that carborundum is a very poor conductor as compared with carbon and graphite. A pressure of 100 volts may be applied to a piece of carborundum without causing a very considerable amount of current to flow, though there will be a certain amount of current as shown by the fact that the carborundum crystals may heat. A piece of graphite of similar size will carry a much larger quantity of current for the same pressure, showing that, at moderate temperatures at least, the conductivity of carborundum may be practically neglected, as Mr. Fitz Gerald has suggested.

PRES. RICHARDS: I should like to ask Mr. Fitz Gerald, where he speaks of the efficiency of this furnace, whether he has made any calculations as to the percentage of the efficiency which is reached in the graphite furnaces.

MR. FITZ GERALD: No, I have not made any calculations of the efficiency. Conditions are very complicated. I have tried to make such calculations, but gave it up as hopeless.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 17, 1903, President Richards in the Chair.

ADVANCES IN ELECTRO-METALLURGY OF IRON PRODUCTION.

By Marcus Ruthenburg.

At the last meeting of the Society, which unfortunately I could not attend, through the courtesy of our secretary a paper was read for me upon the "Electro-metallurgy of Iron and Steel." In the discussion which followed the reading of the paper, as well as in the technical press of this country and Europe, there has been a mild skepticism as to the possibility of electric smelting competing with the blast furnace in the production of iron and the further reduction of this iron into steel by the Bessemer converter or the Siemens furnace.

It is noticeable, that without exception, these criticisms have been, not by men practical in the manufacture of iron or steel, but by that class of scientific dilettante who assume with an array of figures and formula to prove with equal facility either side of a question that their sympathies happen to be enlisted upon.

The truth of the blast furnace is that it is a highly economical device for accomplishing its end and will continue to be so until methods be found that will perform its functions for less money.

Some classes of ore may now be more cheaply reduced to metal by other means than the blast furnace, making a product whose analysis cannot be produced in the blast furnace at all. Given a magnetic ore carrying gangue, sulphur and phosphorus in prohibitive quantity for making good steel economically, such ores find no market tributary to the blast furnace.

On the other hand such ores may be crushed, magnetically concentrated, electrically smelted and produce the best of steel at a price which can compete with an ideally situated blast furnace.

In last year's paper I made the assertion that "the work of the electric furnace was performed upon a ton of ore with something less than 500 K. W. Hs. of energy."

Upon this basis one of our learned members accorded me an

efficiency of 83 per cent, which he followed up by saying was impossible. In truth at that time I was doing 10 per cent better than that, or an efficiency according to his figures, of 91.3 per cent.

To-day I am prepared to report to you that I am doing the same, but better work, with one-half the K. W. Hs. reported to you last year, and it is with a spirit of some amusement that I contemplate what efficiency I am attaining to-day, assuming always that upon the basis of 500 K. W. H. per ton I was entitled to an efficiency of 83 per cent. Three problems have presented themselves for solution, in the conduct of my work; first, the power required to agglomerate and sufficiently heat for subsequent reduction; second, the regulation of the size of the agglomerated particles; and third, the amount of reduction of the agglomerated material.

The status of those three problems to-day is that a ton of ore is being agglomerated with an expenditure of about 250 K. W. H.

The size of the product is under perfect control.

The reduction is being made absolute. Inasmuch as the only function of the electric current is to agglomerate the dusty particles into coherent masses without binder or flux, and to convey a sufficient quantity of heat to the ore in the soaking pit, to permit the reducing agents to perform their functions, it will be readily comprehended that the heat and current losses due to maintaining a molten mass are lacking.

DISCUSSION.

Mr. C. J. Reed: I should like to ask Mr. Ruthenburg if he has made any calculations as to the efficiency of the process. On what basis are these calculations made? What is the number of calories assumed to be required to produce the temperature necessary in a pound or a ton of material?

Mr. Marcus Ruthenburg: When you come to discussing calories and efficiencies, I confess plainly, that is beyond my depth. The only things I base my statements on are, that with the instruments that the common, everyday, working electrician uses, I know the results that I have accomplished. I weigh my

product, I weigh my ore, and read my wattmeters; and it is of small moment to me whether I use 1,000 calories or 10,000 calories, or any other number, as long as I get the product with a certain expenditure of money. I fancy there are those in the room who have taken that part up and will enlighten you on it more than I possibly could. There is one point it is well to call to the attention of the lay mind as far as the metal iron is concerned; and that is, iron is peculiar in the fact that its reduction by hot CO takes place at temperatures that are entirely foreign to the reduction of any other metal with which I am familiar. A temperature but little above that of boiling water is sufficient for a reaction to start between CO and the various oxides of iron. It may be the case with others, but I am not familiar with them. That is one reason why the electrical efficiencies are approachable that I reach. I don't apply the current to melt the ore and heat it to an abnormal temperature, owing to the fact that the reduction of iron ore takes places at those low temperatures through the action of hot CO.

Dr. George P. Scholl: What is the analysis of this material as it comes out as the finished product?

Mr. Ruthenburg: By the analysis I presume that Doctor Scholl refers more particularly to the content of iron.

Dr. Scholl: What becomes of the metalloids, *e. g.*, phosphorus and sulphur?

Mr. Ruthenburg: The phosphorus is controlled entirely through the preliminary cleansing of the ore. My work has been devoted entirely to the handling of magnetic ore. In fact, nothing but magnetic ore will work in the peculiar type of furnace that I use; and as far as sulphur is concerned, a very peculiar reaction takes place, in the absence of carbon. Sulphur is absolutely eliminated. It is simply through the high temperature of the electric furnace, a reaction of Fe and its various combinations with O and FeS_2—a reaction of driving off sulphurous anhydride and giving metallic iron. You are getting your oxygen from iron oxide, instead of the oxygen of the atmosphere as in a roast. That is its relation to sulphur. As far as the phosphorus is concerned, it plays the same part in the electric furnace that it does in the blast furnace or in an ordinary steel hearth (excepting a basic

hearth with lime). There is no phosphorus eliminated at all in them or in the electric furnace. Whatever phosphorus you remove, as a general thing (it being a constituent of the gangue of the ore), is removed in the original magnetic concentration. As far as the analysis of iron is concerned, I have had results varying from only 5 per cent or 10 per cent reduction up to as high as 92 per cent; the product of the soaking pit would come out 92 per cent of metallic iron, which I have considered fairly good work up to the present time.

Dr. Scholl: How about the carbon? What is the condition of the material?

Mr. Ruthenburg: The condition of the material? In the first place I ought to explain the form of the furnace. I remarked a while ago that it was only suitable for the use of magnetic ores; and the reason is that the smelting is done in a magnetic field, and the magnetic field plays no other part in the smelting operation than holding the ore until it is melted into lumps, or until its dusty form has been broken up, so that it will no longer pack and impede the flow of gas. The poles of the magnet are surrounded by a pair of water-cooled, carbon-covered cylinders. The carbon plays no other part than, should the furnace flash, it prevents the iron oxide from being welded to the rolls. The carbon covers do not get hot; the rolls are kept partially filled with water, which is continually fed in like a water jacket and overflows; and as the rolls slowly revolve around the magnetic poles the moment that the particles of iron have been held as a bridge and molten, they drop out, from weight or from loss of magnetic permeability. These molten particles drop into the soaking pit, and in dropping, if the top of the charge of the pit is close enough to the rolls, part welds to part; but it makes a friable, permeable, granular mass that is freely permeated by the gases by which reduction is accomplished. An analysis from a sample taken immediately upon dropping from the rolls will show anywhere from 2 to 5 per cent more iron than raw ore that went in; showing that some oxygen may be eliminated while between the rolls, too. What reaction that would be due to I am unprepared to say. It goes into the pit with not over 5 per cent elimination of oxygen, and the balance of the oxygen is removed in the pit through the action of hot CO.

MR. REED: I would like to ask for an explanation of the fact, as stated by Mr. Ruthenburg, that in this process the sulphur is entirely eliminated. Is it due to the fact that the sulphur is not reduced and cannot remain as a sulphide?

MR. RUTHENBURG: Within the last few months I have taken up the reaction of the sulphur, in the peculiar furnace that I use, and it attracted more than passing attention. While ordinarily the magnetites that I have had to work upon contained not to exceed 1 per cent of sulphur (which relatively is small), its absolute elimination was a point that required attention. I then attempted the reduction of sulphide and oxide, by mixing the proper proportions and attaining the temperature suitable to the reaction, the elimination of 40 per cent of the sulphur from the sulphide is almost complete. It is due to the oxygen of the iron oxide and not due to the oxygen of the air. If you do not raise the temperature high enough, you simply get a fused magma in which the sulphur is reduced to about 5 per cent at ordinary temperatures; but the moment it is subjected to the temperature of the electric furnace it is almost completely removed.

MR. COWLES:—A like reaction occurs in the metallurgy of lead and in the metallurgy of copper. Lead sulphide and lead oxide heated together give metallic lead and sulphurous acid. Likewise, copper oxide heated with copper sulphide in the proper proportions give metallic copper and sulphurous acid.

I have had the pleasure of witnessing Mr. Ruthenburg's furnace and watching its operations. I have also measured its consumption of energy. One thing that impresses me as very favorable to it is the fact that the only product that drops into his soaking pit is the iron oxide after it is fused. Before it is fused it is magnetic and is held in the magnetic bridge of the furnace, and only such particles as become fused become non-magnetic and drop; so it is that he is continually charging into his soaking pit, iron oxide that has been heated hot enough to have fused. After this has accumulated in his soaking pit it furnishes a heated mass practically within a retort or chamber through which he can pass his reducing gases. Early in the seventies, Sir William Siemens and Sir Lowthian Bell experimented upon the reduction of iron oxide with hydro-carbon gases and carbon monoxide, and it was found that these gases caused a reduction of iron oxide

to take place at very low temperatures; but, of course, the higher the temperature the more rapidly the reduction goes on. It was found impracticable to pass heat through the walls of the confining chamber and effect the reduction in this manner. In the case of Mr. Ruthenburg's furnace he is in effect, applying his heat or energy within his retort, and he does not have to pass it through the walls of a chamber that are bad conductors for heat. His ore drops into his soaking pit highly heated and in a condition to be easily permeable by gases. A moderate application of heat externally will eliminate radiation from his problem and then, by the passsage of heated hydro-carbon gases through his charge, he contemplates securing complete reduction of the magnetite ores he is working with. It seems to me that one may look for his process to develop into a successful commercial process, especially in locations where water-power is cheap and coke is expensive. Carbon monoxide comes off from the top of the soaking pit. This gas can be carried around the sides of his soaking pit and be burned, and thus contribute largely towards preventing loss of heat from within by conduction and radiation. I should judge that the material that drops into his pit is heated to about 1,200 or 1,300 degrees Centigrade. Last night I made a calculation of the heat energy required for reducing magnetite. Mr. Ruthenburg states that by his process he can agglomerate a ton of pulverized magnetite with an expenditure of about 250 K. W. hours. I have seen him do this with a much less expenditure of power. This statement is equivalent to saying that one electric H. P. hour will agglomerate 6 pounds, or 2,718 grams of pulverized magnetite, or Fe_3O_4.

One electric H. P. hour is equivalent to 644,000 small calories. Assuming no loss in heat energy, this heat is delivered in Mr. Ruthenburg's furnace to 2,718 grams of Fe_3O_4, according to his statement, or $644{,}000 \div 2{,}718 = 237$ calories delivered to each gram. The specific heat of magnetite is 0.154, or two-thirteenths that of water. Hence, if to each gram of magnetite there is given enough heat to raise one gram of water 237 degrees Cent., it would raise each gram of his magnetite 6.5 times 237 degrees, equaling 1,540° C. This is under the assumption that the specific heat of Fe_3O_4 does not alter at high temperatures. In three gram-molecules of Fe_3O_4 there are 696 grams. Hence, according to

Mr. Ruthenburg's statement, he is delivering to each three gram-molecules, $237 \times 698 = 165{,}426$ calories.

This latter figure may be compared to that theoretically required in the reduction of 3 molecules of magnetite by methane or marsh gas (the most common hydrocarbon), under either of two assumptions: first, that the products of the reaction come off as carbonic acid and steam, or secondly, that they come off as carbon monoxide and steam.

Taking the first assumption, the reaction would be

$$3\ Fe_3O_4 + 4\ CH_4 + 4O = 9\ Fe + 4\ CO_2 + 8\ H_2O$$

The heat required to dissociate 3 Fe_3O_4

$270{,}800 \times 3 = 812{,}400$ calories.

The heat required to dissociate 4 CH_4

$18{,}900 \times 4 = 75{,}600$ calories.

Total heat absorbed, 888,000 calories.

Heat evolved by 4 molecules of CO_2

$96{,}900 \times 4 = 387{,}600$ calories.

Heat evolved by formation of 8 molecules of H_2O as steam, $58{,}300 \times 8 = 466{,}400$ calories.

854,000 calories.

The difference between the heat absorbed and the heat evolved, or that required for the reaction

$888{,}000 - 854{,}000 = 34{,}000$ calories.

It will be noted that this is less heat energy than that which Mr. Ruthenburg claims to be delivering into his soaking pit. If we make the same calculation under the second assumption, which involves his oxygen passing off in CO, then the reaction would require 305,600 calories, nearly twice as much energy as Mr. Ruthenburg claims to deliver in his soaking pit.

Mr. Ruthenburg contemplates preheating his reducing gases before their passage through his soaking pit, and while the electric energy is probably not sufficient to reduce the full amount of material that he agglomerates, there is available to his process, the heat that will be carried into his soaking pit by his heated

reducing gases. Those who have criticized his process may not have fully understood this latter phase of the same.

Mr. F. M. Beckett: Did you find that sulphur was entirely eliminated when carbon was present in addition to that on the rolls?

Mr. Ruthenburg: In the presence of carbon the sulphur is eliminated to but a very small extent. It seems to be essential that carbon shall be absent to accomplish the elimination of sulphur. Upon the reference by Mr. Cowles to the reaction practiced in the lead and the copper industries, the reaction is to some extent different, and the relation between iron sulphide and iron oxide, lead oxide and lead sulphide, copper oxide and copper sulphide. As I remarked before, I cannot go into the technicalities of the atomic relations of them because I do not know how, but when it comes to the practical work I have handled both those operations. With lead it is the old Corinthian process of roasting one-half of the charge, and the nearer that roast comes to being a dead sweet roast, the more thorough the reaction will be. That is mixed with the remaining half of the charge unroasted, and the reaction produces SO_2 and throws down metallic lead from both sides of the charge. With copper, the copper men thirty years ago took up this reaction of lead: they attempted to do the same thing with copper, and with careful roasting it was just as successful with copper ores as with lead ores. These things I know from practical experience, but just what the reactions are, other than what I have stated, which result in the production of SO_2 and metallic lead or copper, I don't pretend to know. But with the reaction of the iron sulphide and the iron oxide, *that* does not take place at the ordinary temperatures at which these reactions of copper and lead do. The reactions of copper and lead take place upon the hearth of a common, ordinary reverberatory furnace. The temperature must not be too high. On the other hand, with the iron oxide and iron suphide it seems to be absolutely essential that the temperature shall be very high and one that is not attainable through ordinary carbonaceous combustion.

Mr. Beckett: I have performed many experiments on the reduction of iron oxide by iron sulphide with the object of making metallic iron. These experiments were carried out at various temperatures up to at least 2,000° C., with and without the pres-

ence of carbon—carbon having been eliminated even at the electrodes—and, although I have found considerable reduction of the sulphur, I have never been able to obtain the metal free from sulphur. I came to the conclusion after several months work that the complete reaction was not possible. I do not think it fair to assume that this reaction will take place, because that between lead oxide and lead sulphide or copper oxide and copper sulphide does, the thermochemical data not being nearly so favorable as it is in the cases of lead and copper; and I believe in Schnabel's "Metallurgy" it is stated that the reaction between nickel oxide and sulphide will not produce metallic nickel. I should think iron more closely allied to nickel than to copper or lead. As this reference was found after some months of experimental work with iron, it seemed fair to conclude that metallic iron free from sulphur cannot be produced by the reaction between oxide and sulphide. With certain fluxes, however, the sulphur can be reduced to a low figure. I think the elimination of sulphur more likely due to other reactions.

Mr. Ruthenburg: The work we have been carrying on, on the oxide and sulphide, does produce metallic iron, but it contains some sulphur—I don't question that, at all; but the amount of sulphur is very small—so small that the reactions for testing for the metallic iron demonstrate its absolute presence there in overwhelming quantity, as true metal. In the presence of carbon I have not been able to do that. I cannot eliminate the sulphur in the presence of carbon, but without the carbon the reaction does take place, at a sufficiently high temperature.

President Richards: I think the point is, that Mr. Ruthenburg has been working with ores which are comparatively low in sulphur, and while the sulphur is not absolutely eliminated to the last trace, yet some of it is eliminated. Mr. Ruthenburg has not been working with iron sulphide.

Mr. Ruthenburg: More lately I have.

The Chairman: But in that case you didn't obtain a product entirely free from sulphur.

Mr. Ruthenburg: No, not commercially free.

Pres. Richards: But in the case of magnetic ore, which is itself low in sulphur, some sulphur, or enough sulphur, is eliminated during the reaction to give a product commercially free

from sulphur. With Mr. Ruthenburg's permission I will allude to the fact that, when I read his paper at the meeting of the Society last fall, I commented on his statement as to the efficiency which he had attained—taking his process as a melting process—for agglomerating magnetite together. I did not know then the temperature to which it was heated, but assuming that it was heated to the temperature of a steel bath, I calculated from the data then given an efficiency of 83 per cent. I do not remember as having stated that to be impossible, but that it was a high efficiency. With the lower temperature that Mr. Cowles states, 1,200°, of course the calculated efficiency would be reduced in the proportion of 12 to 15. The comment which I made then on the commercial applicability of the process was concerned with the manner in which Mr. Ruthenburg proposed it. His proposition then was to make his process an agglomerating process: to agglomerate the material for subsequent reduction in the blast furnace, and he made a comparison of the cost of agglomerating it in the electric furnace with the cost of briquetting it, as is the usual manner for reduction in the blast furnace, and I then stated that the calculation seemed to show that the cost of agglomerating it was much higher than the cost of briquetting it for subsequent reduction in the furnace. Mr. Ruthenburg's remarks now, I think, apply to the commercial applicability to the further reduction of the heated material by carbonic oxide gas, and not to its reduction in the blast furnace, so that I have not any strictures at all to make upon the commercial possibility of the reduction of the ore in this way, by means of carbonic oxide gas.

Mr. Ruthenburg: My first work, which was begun several years ago, did, as Dr. Richards says, relate almost exclusively to a preliminary treatment for the blast furnace. That work is still being contemplated for certain ores as a preliminary treatment for ore for a blast furnace, and has to be figured upon its own basis. I know of ores on which an expenditure of $1, or even $1.50 per ton, as preparatory to the blast furnace would be entirely legitimate, and would be good business practice. I know of other ores that an expenditure of 25 cents per ton would preclude its adoption. As applied to the smelting of iron ores there has always been an assumption that electrical energy costs a great deal of money. There has also been an assumption that water-

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power must always be the cheapest source of electrical energy. Both of these propositions are sometimes wrong, and it depends entirely upon what your kilowatt hour costs you as to whether you can apply it to the preparing of ore for blast furnaces or not, and, of course, every different location would be figured upon a different basis and with different data applying to that cost. You can go into the coal regions of Pennsylvania, where you can get your coal for a nominal price, and with large unit compound-condensing engines, or preferably large unit gas engines, a kilowatt hour can be generated at a price that makes it a very desirable proposition. With water-powers of large magnitude, entirely from a commercial standpoint, where the current can be obtained at a price in keeping with what it is worth, a man is invited to go there. If he cannot get water-power at such price as appeals to him, as a business man, of course he goes where he can get power cheaper. The whole point I make is that the unit value of the kilowatt hour, especially among those who have occasion to generate and dispose of their product as kilowatt hours, is exaggerated as to what it costs. Upon the basis of $2.24 per ton for coal and ¼ cent per kilowatt hour (because that happens to be the mill per pound price that prevails in some sections of Pennsylvania), even a preparation for the blast furnace on a basis of 500 kilowatt hours—let alone the later figure of 250 kilowatt hours—the work can be done upon the ore for 62½ cents. The owners of some ores will stand that and be glad to pay it. Some ores cannot stand it, and, of course, when they cannot stand it, it is not a commercial proposition, and the work is not done. If the figures work out in an appealing way to the man who operates the blast furnace, he wants the work done. My carrying the work past the point of preparation for the blast furnace came about in a peculiar way. I happened to be interested in a mass of ore at a time when I was consuming 450 kilowatt hours to do the work upon it. The ore would not stand the charge of $1.12, and I naturally felt very down-hearted over the prospect of having to quit upon that work. I knew that various people in Europe had attempted the reduction of ore directly into steel, electrically. My information led me to believe that from 3,000 to 4,000 kilowatt hours per ton were consumed in doing that work, and I could not comprehend—(I suppose my

mental processes happened to be dense at that time)—but I couldn't exactly comprehend why it was that in a magnetic field I could melt with 450 kilowatt hours, and through my conclusions of some of the relations of calories and chemical reactions I could not understand why it should take the difference between 450 kilowatt hours and a minimum of 3,000 kilowatt hours for the simple act of reduction, if I only consumed 450 in the *heating* of the ore. That led me then, as a *dernier ressort,* to adding a reducing material in the form of charcoal dust, and later in the form of hot CO to the ore. I was surprised to find that I consumed 450 kilowatt hours again, and I was still wholly in the dark. I knew that in reducing I was performing useful labor, and I could not understand where the useful labor came from. The truth of the matter was, I was expending as much energy in heating the raw ore as was required to do it when I added a reducing material, and whatever energy was required for the reduction, came from residual heat and the reducing material. That was what led me to take up the steel end of it.

President Richards: I congratulate the Society on having had this subject before it, and particularly by Mr. Ruthenburg, as being one of the pioneers in this country in the electrical treatment of iron ores. There is no doubt at all from the developments that we see abroad and from what we feel is going to happen in this country, that the electrical furnace and electrical methods are going to have a large place in the metallurgy of iron and steel. They have already found a place in the manufacture of the finer qualities of steel; and it is perhaps a question of only a few years until they will be largely applied in this country and all over the world. Then it will develop into probably the largest electrochemical industry. We are fortunate in having had this subject before us so ably presented and so thoroughly discussed.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 17, 1903, President Richards in the Chair.

A PRACTICAL UTILIZATION OF THE PASSIVE STATE OF IRON.

By Charles F. Burgess

In what may be considered the ancient literature of electrochemistry the fact was pointed out that iron and steel may be made to assume that peculiar condition known as the passive state by employing the material as an anode in suitable electrolytes. Among such solutions are sodium nitrate and various other soluble nitrates.

Upon assuming the passive condition, the iron no longer becomes attacked by the anode products, oxygen being liberated, and the metal acting towards the solution as would an anode of platinum. The passive state thus produced was held to be, and probably is, the same condition which iron assumes when immersed in concentrated nitric acid, the passivity probably being due to the same causes in both instances. Whether this peculiar condition is the result of the formation of a coating of iron oxide or of nitrogen oxide, or of some other material, is a disputed question, a discussion of which is foreign to this paper.

While this peculiar behavior of iron, when used as an anode material, has been known for many years, it is only quite recently that it has been made use of in an industrial way.

Some years ago we developed in our laboratory a process for removing brass from steel tubing, the brass having been left on the outside of the tubing as a superfluous material during the brazing process. An improvement in the method of brazing employed extensively in the manufacture of bicycles consisted in dipping bodily a portion of the frame to be brazed into a bath of melted spelter, which was covered by a suitable flux. By this operation not only was the brazing effected within the joints, but a thin layer of brass adhered to the outer walls of the tubing, so that it became necessary to remove this layer in preparing the frames for receiving a coating of enamel. This was effected for some time by filing, a process which had the disadvantage of

entailing a large amount of labor and frequently of damaging the thin tubing, as some of the iron was removed as well as the brass.

An attempt was made to employ an electrolytic stripping process for removing this brass, but, upon trying a great many electrolytes, it was found that the iron itself tended to corrode much more readily than did the copper which enters into the constitution of the brazing spelter; and the problem resolved itself into finding a solution which would dissolve the copper, but in which the iron would not corrode.

Iron has a position considerably above copper in the electrochemical series of elements, and where two different metals are in contact the natural tendency is for the more electropositive one to go into solution with the greater ease. The idea presented itself of making the iron more electronegative than the copper by causing it to assume the passive state, and upon using the sodium nitrate solution in which this state could be developed it was found that the brass could be completely removed and the iron left intact.

This method of electrolytic stripping was installed and operated with success in various factories, and is now an important adjunct to the dip-brazing method. This same electrolytic stripping process may be applied equally well in removing silver, lead, tin and other metals more electronegative than iron from an iron surface. Nickel cannot be removed in this way, however, since nickel, as well as the iron, assumes the electronegative or passive state.

In some correspondence with the Patent Office it was claimed that while the iron might assume a passive condition, becoming coated with a resistant film of iron oxide, it could not be considered as becoming electronegative. For the purpose of determining this question, some measurements of single potentials were made upon iron before and after it had assumed its passive condition, and the results showed clearly the manner in which these metals behaved while being subjected to the action of the current. The measurements were made by means of a normal electrode of the "calomel" type, the potential of which was taken as — .56 volt. The metal whose single potential was to be tested was placed in the electrolyte and the potential measured before applying an electrical pressure, and also after currents of different values had

been caused to flow. It was found that up to a certain limit the single potential varied in accordance with the current density. These values at different current densities were determined by a specially-constructed switch, which broke the current and immediately connected the electrode with the normal electrode circuit for an instant, long enough to determine the direction of the movement of the meniscus of a capillary electrometer used as a zero potentiometer instrument. In the following tables are given the results of some of these measurements:

I.

Solution = normal sodium nitrate.

Anode = iron, — area = 3½ sq. in.

E. M. F. between iron and solution before passage of current = + .07.

Applied Pressure Volts	Current Amp.	Single Potential Volt
.2	.006	+ .06
.4	.022	+ .032
.5	.032	— .01
.8	.085	— .053
1.2	.175	— .11

The above test was made in solution containing no $NaNO_2$. Measurements made as rapidly as possible.

II.

Solution = normal sodium nitrate.

Iron anode = area 3.5 sq. in.

E. M. F. between iron and solution before passage of current = + .002.

Applied Pressure Volts	Current Amp.	Single Potential Volts
.3	.005	— .138
.5	.015	— .138
.7	.034	— .138
1.	.080	— .138
1.3	.130	— .166
2.2	*.160	— 1.89
2.8	.130	— 1.97

* When pressure of 2.2 volts was first applied, current was .16 ampères, but it quickly dropped to .026 ampères, due to assumption of passive state by the anode as shown by the great change in E. M. F. of the plate.

III.

Solution = normal sodium nitrate, into which was placed a small amount of $NaNO_2$.

Anode = iron plate, area = 3.5 sq. in.

E. M. F. between iron and pure nitrate solution = + .28 volt.

E. M. F. between iron and pure nitrate solution, with addition of $NaNO_2$, = + .23 volt.

E. M. F. of same after standing five minutes = .09 volt.

Applied Pressure Volts	Current Amp.	Single Potential Volts
.3	.0005	— .221
.5	.001	— .452
.7	.002	— .645
1.0	.003	— 1.04
1.3	.004	— 1.21
2.2	.070	— 1.46
2.9	.172	— 1.63

On remaining some time with this current flowing, the E. M. F. of anode rose to — 1.94 volts.

IV.

Solution = same as above.

Anode = sheet copper 3.5 sq. in. area.

E. M. F. between copper and electrolyte = — .238 volt.

Applied Pressure Volts	Current Amp.	Single Potential Volts
.3	.0005	— .421
.5	.003	— .49
.7	.005	— .56
1.0	.023	— .67
1.2	.043	— .64
2.4	.300	— .658

It was noted that the single potential of iron immersed in a sodium nitrate solution before the current passed was in the neighborhood of + 0.2 volt. In other words, a potential was set up toward the solution in the same direction, but of less magnitude than would be produced by zinc. By causing the current to pass from the iron electrode, however, this potential quickly became negative, and increased rapidly in negative value until potential

as high as — 2.0 volts could be obtained under certain conditions. This potential of iron, when in the passive condition, is considerably higher than the single potential of platinum, and consequently in this condition may be considered as electronegative to that metal. Its potential is approximately equal to that of the peroxide plate of the lead storage battery.

Copper, on the other hand, as shown in Table IV, does not change its contact electromotive force in anywhere near the same degree. The maximum electromotive force of copper was — .65 volt, and it will be seen that the iron may readily be made much more electronegative than this value.

It was found that the iron did not assume the passive condition when used in sodium nitrate solution freshly prepared, but that this condition was developed after the current had flowed for some time. This fact led to the conclusion that the solution underwent some chemical change which was favorable to the passive state. In the electrolysis of a sodium nitrate solution under the above conditions sodium is liberated at the cathode, uniting with the water to form sodium hydroxide, and the hydrogen which is thereby set free reduces the sodium nitrate to nitrite.

Table I gives the results of a test upon a sodium nitrate in which there was present none of the nitrite.

Table II gives the results of a test with sodium nitrate after operating some considerable time, and Table III gives the results of measurements upon a sodium nitrate solution in which had been added previously a small amount of nitrite. It will be seen in the last case that the iron assumes the electronegative condition with a greater rapidity and at much lower current density.

In removing brass from iron, the current should remove it at the approximate rate of 1 gram per ampère hour, provided that all of the current enters the solution from the brass and none of it utilizes the iron as an anode surface. To determine how nearly this is the case when iron and brass in contact are exposed simultaneously to the solution, an experiment, illustrated in the following diagram, was performed:

A brass and an iron anode, each having dimensions of 1 x 2.75 inches, were immersed in a sodium nitrate solution. Each was connected through the ammeter to the same source of current. It was found that on first closing the circuit almost all of the current passed through the iron anode, but after operating for a few seconds the iron became passive, after which the brass took all of the current, the amount passing through ammeter, A, being so small as to be hardly detected. The following table gives the results of measurements:

Time	A	A_1	V
11.50	.15	.75	3.7
11.51 : 30	.70	0	3.7
11.55	1.1	0	3.7
11.56	1.85	.12	5.4

Gas liberated on iron.

By using very high current densities, however, the iron may begin to conduct a small portion of the current, thus causing a liberation of oxygen on the iron surface. From these tests it was shown that the current has a high efficiency in the removal of the brass, and a practical trial has demonstrated that a small percentage only is wasted by flowing from the iron surface, provided the solution be maintained in good working condition and the applied electrical pressure be kept within suitable limits.

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DISCUSSION.

Mr. C. J. Reed: The position of lead is higher in the scale than iron, as far as its electropositive character is concerned. If we were to remove brass or copper from lead in a similar manner the result would be to cause the formation of lead peroxide, and then we should get the same result as you get with iron, the coating of lead peroxide being highly electropositive. I want to ask whether you would consider it proper to say that was due to a passive state of the lead?

PROF. C. F. BURGESS: I am of the opinion that the so-called passive state of iron is analagous to that condition which lead assumes when it becomes coated with a lead peroxide coating. A reasonable explanation of the passive condition of iron is that it becomes coated with a certain iron oxide, which is electronegative, just as is lead peroxide electronegative as compared with the lead. There is opposition to this view, from the fact that there is not apparent upon the iron surface such a film. If, however, the iron be used as the anode for a considerable length of time a black coating is formed which is readily visible to the eye.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1903, President Richards in the Chair.

AN EXPERIMENT ON THE ELECTROLYTIC DETERMINATION OF THE BASICITY OF ACIDS.

By Ivar Juel Moltkehansen, Diplom Ingenieur.

The physico-chemical methods referred to in the above title have proved of the highest value in many cases where complex acids of doubtful basicity are in question. Some time ago I made some investigation on these lines, treating one of the most difficult problems of inorganic chemistry, the constitution of the metaphosphoric acids. I may later on come back to the more chemical part of my work, and shall here only shortly recall how Thomas Graham (Pogg. Ann. 32, 61) illuminated this field when, in 1834, he published his "Examination of the Arsenic and Phosphoric Compounds, as well as of the Modifications of Phosphoric Acids." Graham gave the right formula for ortho-, pyro- and metaphosphoric acids in his essay, and he also, for the first time, showed the difference between the two latter acids. Only the metaphosphoric acid, simplest in its constitution, has shown itself capable of forming complex compounds, known as mono-, di-, tri-, tetra- and hexametaphosphoric acids. Fleitmann (Liebig's Ann., 65) and Lindbour (B. deutsch. ch. Ges. 8, 1875) have studied these metaphosphates, as well as Madrell, Tammann, Glatzel, von Knorre and others.

The important question, of ascertaining the constitution of the different metaphosphoric acids, could only be solved by analysis of their double salts, as the determination of their vapor density is not practicable, owing to the decomposition of the metaphosphate vapors, even at a low pressure. The metaphosphates are dissociated in a water solution, and their molecular weight cannot, for this reason, be determined by the methods of lowering of the freezing point or the increase in the boiling point. They are not soluble in solvents containing no hydroxyl, such as benzol or chloroform. A decision as to the constitution of the water-soluble metaphosphates is, however, possible, according to their con-

ductivity for the electric current, as set forth in the following report.

I first turned to *dimetaphosphoric ammonium,* preferring Glatzel's formula for preparing this compound (Dissertation, Wuerzburg, 1880) to Fleitmann's (l. c.).

Cupric chloride was treated on the steam bath with concentrated phosphoric acid in small excess, and orthophosphate of copper results. On the sand bath, by increasing the temperature (up to 400° C), the decomposition was completed, as shown by the following equation: $CuCl_2 + 2H_3PO_4 = Cu(PO_3)_2 + 2HCl + 2H_2O$.

This copper dimetaphosphate was washed with water, after having been powdered, and the filtrate gave no reaction for hydrochloric acid. The washed salt was treated with an ammonium sulphide solution, with a small excess of ammonium hydrate (Fleitmann, Pogg. Ann. 78, 251), which increases the rapidity of the double decomposition, as ammonium hydrate is a good solvent for copper dimetaphosphate. The excess of ammonium sulphide was driven off on the steam bath (care being taken not to raise the temperature high enough to decompose the ammonium dimetaphosphate), and the salt was brought to crystallization by alcohol.

Fleitmann got his salt free from water of crystallization. Glatzel's ammonium dimetaphosphate had 4 mol. water going away at 200° C. My analysis gave on 0.4919 gr of ammonium salt a total loss of 0.1914 gr, equaling 38.94 per cent. Theoretically, the salt with 2 mol. water of crystallization contains 38.26 per cent ammonia and water.

0.2176 gr of the salt showed by titration, after distillation, a content of 0.03225 gr NH_3, which equals 14.85 per cent. Theoretically there is in $(NH_4)_2P_2O_6 . 2H_2O$, 14.78 per cent NH_3.

The salt is then a somewhat moist ammonium dimetaphosphate, with 2 mol. water of crystallization. A second trial produced a salt of the same constitution (NH_3 + water = 38.85 per cent), although no alcohol was used to bring it to crystallization. And a second crystallization of this product also gave the same crystalline mass of white ammonium dimetaphosphate, with even some less (38.15 per cent) NH_3 + water. The difference was 61.85 per cent, determined as P_2O_5, which checks well with the theoretical amount, 61.74 per cent, P_2O_5 for $(NH_4PO_3)_2 . 2H_2O$.

The results of the analysis are labeled: $[(NH_4PO_3)_2.2H_2O]$ which contains

	Theoretically	Experimentally		
		I	II	III
$(NH_4)_2O$. $2H_2O$	38.26	38.94	38.15	38.85
$2NH_3$	14.78	14.85	....	14.38
$3H_2O$	23.48	24.09	....	24.47
P_2O_5	61.74	(61.06)	(61.85)	(61.15)
	100.00 per cent			

The problem before me was now to examine the equivalent conductivity of this compound in an electrolytic cell, and in suitable dilutions to draw new conclusions as to the constitution of the salt according to the empirical formula given by Ostwald. The determinations of the conductivity of the solutions for the electric current were all made according to the method of Kohlrausch, founded on the principle of the Wheatstone bridge, in which a telephone replaces the galvanometer and an alternating current is used to avoid the injurious polarization of any gases formed on the electrodes. The solutions were placed in the carefully-cleaned resistance cell of Arhenius, and the temperature kept constant at 25° C in an Ostwald thermostat.

The resistance of the copper wires used was determined, and found to be 0.060 ohm, a value too small to be taken into consideration.

The capacity *(k)* of the resistance cell had to be determined before the measurement of the conductivity of the solutions could be undertaken. This capacity is, according to Kohlrausch, measured with a $\frac{n}{50}$ potassium chloride solution, the conductivity of the latter being 129.7 at 25° C. The formula for this calculation, as given by Ostwald, is

$$k = \mu \times \frac{b}{a} \times \frac{w}{v}$$

in which v equals 50,000 for the $\frac{n}{50}$ solution, and

$$\frac{\mu}{v} = \frac{129.7}{50000} = 2.594 \times 10.^{-3}$$

This value is given in Siemen's units, and, to transfer to ohms, has to be divided by 1.063, as 1 ohm = 1.063 Siemens units. I found $\frac{b}{a} = 0.972$ for $v = 50$ as the result of several determinations. This gives

$$k = 48.65 \times 2.594 \times 10^{-3} = 0.1262.$$

It was further important to know the resistance of the distilled water used, because the same has considerable influence on the value of the conductivity at the highest dilutions. It was then found that the purity of the water was not constant, but varied between 16,000 and 38,000 ohms. It seemed, for this reason, expedient to make up the numerous solutions of one series of experiments of the highest possible quantity of water, the resistance of which was known and controlled throughout the experiments.

By making up the desired $\frac{n}{32}$ solution, the moisture of the salt was considered, so that the weighed and dissolved amount of the salt contained as much NH_4 and PO_3 as a $\frac{n}{32}$ solution of the dried salt. 0.7375 gr of the moist $(NH_4PO_3)_2 \cdot 2H_2O$ was dissolved in 200 cc of water. I always made from this $\frac{n}{32}$ solution the two next following, but, to have a certain control as to the correctness of my solutions, these two solutions, $\frac{n}{64}$ and $\frac{n}{128}$, were made the basis of two parallel series of solutions, thus: from the $\frac{n}{64}$ solution the $\frac{n}{256}$ and $\frac{n}{1024}$ solutions were made, and from the $\frac{n}{128}$ the $\frac{n}{512}$ solutions, etc.

Every value of the conductivity, λ_n, as given in the following table, is the result of three or four different observations with the telephone for the value $\frac{a}{b}$ changed according to the resistance included in the path of the current as it passes through the rheostat in the Kohlrausch-Wheatstone parallelogram. The values of different observations may differ one-tenth or two-tenths of a per cent, and the mean of these readings are here given according to the formula $\lambda_v = \frac{k \times v}{\Omega}$. Where λ_v is the equivalent conductivity of the different dilutions of a gram equivalent of the salt, k is the before-mentioned capacity of the resistance cell, v is the dilution in cc — the amount of cc, wherein one gram equivalent of the salt is dissolved—thus for $\frac{n}{32} = 32{,}000$ and for $\frac{n}{1024} = 1{,}024{,}000$; Ω is a product of the experimentally-found

values $\frac{a}{b} \times R$, and R being the resistance of the rheostat, b and a the two pieces of a measured copper wire. The Kohlrausch telephone is attached to said wire by means of a sliding contact, which, at each observation, is moved back and forth till the minimum of sound is sharply fixed as showing the balance of the system when no current flows through the Wheatstone bridge. From these calculated values for λ_v the conductivity of the water was subtracted, and there results for

λ_{32}	λ_{64}	λ_{128}	λ_{256}	λ_{512}	λ_{1024}
98.12	104.8	109.8	115.0	116.0	116.3

(Fig. 1.)

The difference, $\triangle$, of these values is

$$\triangle = \lambda_{1024} - \lambda_{32} = 18.19.$$

As the result of another series of conductivity determinations, when a somewhat larger amount of the salt was weighed out, 0.806 gr to 200 cc, was found

$$\triangle = 125.56 - 106.06 = 19.5.$$

This determination was carried out in co-operation with Dr. T. Lindeman.

These determinations of the conductivity of the solutions show the acid to be dimetaphosphoric acid, according to Ostwald's law, a result to which Fleitmann also came after having studied the double salts of this acid. The found difference, $\triangle$, may further be compared with the empirical formula of Ostwald-Walden, which formula, for all strongly-dissociated salts at a dilution being near the infinite value, has the form

$$\lambda_\infty - \lambda_v = c_v \times n_1 \times n_2,$$

$$\text{or } \triangle = \lambda_{1024} - \lambda_{32} = n_1 \times n_2 \times c_{32},$$

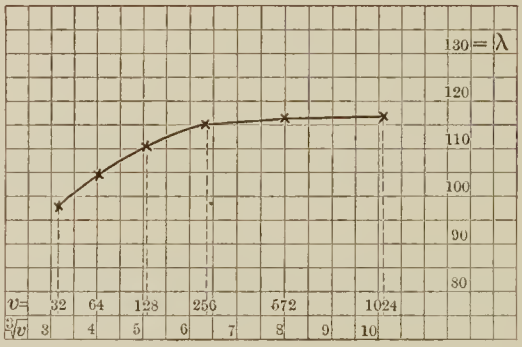
where n_1 and n_2 represent the coefficient of the basicity of the acid and the base. As for ammonium salts $n_2 = 1$, and according to Walden (Z. f. phy. Ch. 1, 259), the value of the constant, c, being a function of the dilution, v, is, on an average, calculated to 10, this formula gives for the basicity of the metaphosphoric acid in question

$$n_1 = \frac{\triangle}{c_v \times n_2} = \frac{18.19}{10} = 1.82.$$

The ammonium metaphosphoric acid has, accordingly, the formula $(NH_4PO_3)_2 \cdot 2H_2O$. The dibasicity of Fleitmann's

dimetaphosphoric acid is thus proved according to the above-mentioned empirical laws.

I further started an experiment to determine the rapidity of the migration of the ions under the influence of the electric current, "Hittorf's Ueberfuehrungszahlen," for my ammonium dimetaphosphate, but my limited time did not allow me to draw the experience gained from the first less successful experiments, which I made with the apparatus designed by Jahn, on to renewed efforts, and Dr. F. Warschauer lately communicates (Z. f. anorg. Ch. XXXVI, 1903) that he also, without success, tried Jahn's apparatus for these determinations for metaphosphates. The modification of this apparatus by Bein is more suitable in this case (Z. f. phys. Ch. 27, 1899, 23).



The determination of the conductivity for the electric current of Fleitmann's dimetaphosphates was earlier undertaken by Tammann (Z. f. phys. Ch. 6, 127), and his values for λ_n give, transferred to 25° C and interpolation,

$$\triangle = 138 - 89.3 = 48.7.$$

F. Warschauer, this year publishing his results (l. c.), got a supposed dimetaphosphoric ammonium with no water of crystalization, thus far in agreement with Fleitmann. Glatzel, as above mentioned, got the salt with 4 mol. water. On determining the electrolytic conductivity of solutions of his salt, Warschauer concludes it to be tetrametaphosphoric acid, as he got

$$\triangle = \lambda_{1024} - \lambda_{32} = 142.9 - 100.2 = 42.7.$$

Warschauer therefore concludes, from his own and Tammann's measurements, that Fleitmann's dimetaphosphoric acid does not exist, but that the acid described as such by Fleitmann and

Glatzel is tetrametaphosphoric acid. My measurements, as here set forth, speak for the existence of dimetaphoric acid in the ammonium salt with 2 mol. water of crystallization, which I produced from the copper metaphosphate. More investigation is called for in this field to explain these varying results, how apparently the same process can give in one case a tetra- and in another a di-metaphosphoric acid.

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A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1903, President Richards in the Chair.

NOTE ON THE ELECTROMETALLURGY OF GOLD.

By W. H. Walker.

The application of electrochemistry to the metallurgy of gold is practically confined to operations based on the use of dilute solutions of potassium cyanide. Although the fact that metallic gold is soluble in solutions of this chemical had been known from an early date, it was at first believed that in order to have the action proceed rapidly enough to be of practical application an electric current must be passed through the solution. In 1867 J. H. Rae, M. D., made an attempt to put this method into practice, and later patented a process for the removal of gold from its ores by the combined action of a "current of electricity and a suitable solvent or chemical," as, for example, potassium cyanide. Twenty years later Simpson proposed a process in which ammonium carbonate was added to the bath as a substitute for the electric current, since it was thought that this chemical would be equally effective in increasing the dissolving power of the potassium cyanide. Soon after this McArthur and Forrest, of Glasgow, published their extensive researches and showed that it was necessary only to employ a dilute solution of potassium cyanide, and to furnish a supply of oxygen in order to have the solution of free gold proceed at a relatively rapid rate even in ores of very low value. These investigators dispensed not only with an electric current in dissolving the gold, but they also eliminated it in getting the dissolved gold out of solution by substituting for electricity the chemical separation of the gold by passing the solution over zinc shavings or turnings.

Metallurgical processes for gold which depend, at least in part, on the electric current may be divided into two classes. Those in which the gold in the ore is dissolved as one operation in leaching vats or tubs, and the dissolved gold subsequently separated electrolytically in a separate piece of apparatus; and second, those processes which provide for the solution of the gold and its simultaneous precipitation in the same piece of apparatus.

Of the first class the oldest and by far the most important is that known as the Siemens and Halske system. The earlier forms of precipitating apparatus used in this method consisted in wooden boxes about 20 feet long by 8 feet wide and 4 feet deep. Copper wires ran along the top of each edge and served as feed wires for the electrodes which were arranged in multiple, the cathode being connected to one side and the anodes to the other. The anodes consisted of sheet-iron plates approximately the cross section of the tank and about ⅛ inch thick. Alternating with the anodes and separated from them by about 1½ inches were the thin sheet lead cathodes supported in wooden frames, having practically the same area as the anodes. Every other electrode was raised one inch from the bottom of the tank, allowing the electrolyte to flow through the apparatus, passing over one electrode and under the next. Owing to the extreme dilution of the electrolyte it was necessary to insure rapid circulation and to employ a very low current density. The pressure necessary when a current density of about .06 ampère per square foot is employed ranges from 4 to 8 volts. The precious metal is held in solution as the double cyanide $KAuCN_2$, which dissociates into the cation K and the anion $AuCN_2$. Thus the gold which is to be recovered by plating on the cathode is continually migrating away from the electrode on which it is to be deposited, and this fact increases the necessity for complete mixing and good circulation of the electrolyte. The reactions taking place at the anode are rather complex, but in general may be considered as first breaking up the anion $AuCN_2$ into gold cyanide, which largely redissolves in the excess potassium cyanide present and free cyanogen which partly is neutralized by the potassium hydrate formed at the cathode, and partly by the iron anode with the formation of Prussian Blue. The potassium ion is liberated on the cathode, and reacting upon the solution reduces the potassium aurous cyanide in the immediate vicinity, plating the gold on the lead sheets and reforming potassium cyanide.

In order that the gold held in the iron cyanides formed at the anodes may be recovered and the electrolyte maintained in a pure condition these electrodes are inclosed in canvas bags.

In a more recent type of apparatus the main tank is divided into six or eight compartments in which the electrodes are placed

parallel to the sides of the tank. The electrolyte flows directly through each compartment over one partition and under the next. The cathodes are formed from strips of thin lead foil hung on galvanized iron wire frames. By means of these frames the cathodes are given an up and down motion, so that as each one strikes the bottom it is slightly bent, forming a bow and thus effectually stirring the electrolyte.

When the lead cathodes have accumulated from 6 to 12 per cent of their weight in gold, they are removed, cupelled and worked up into litharge and gold bullion.

The advantages claimed for electrical deposition over precipitation by zinc are:

1. The use of potassium cyanide solutions more dilute than can otherwise be employed.

2. Less potassium cyanide is destroyed in the precipitating process.

3. The recovered gold is more easily reduced to bullion.

4. More perfect extraction.

The Siemens-Halske process has made great progress on the Witwatersrand gold fields and to some extent also in Australia, but it does not seem able to compete with the zinc process as practiced in America. Great difference of opinion exists as to the relative merits of the two systems; but it is probable that the local conditions obtaining at each plant sometimes favors one system and sometimes the others, so that in general it cannot be said that one method is superior to the other. The current efficiency owing to the small amount of potassium aurous cyanide present must necessarily be very low.

Although many modifications of the Siemens and Halske system in the way of non-corrodible anodes, amalgamated cathodes, etc., have been suggested, we do not know that any marked improvement in the process has followed their introduction.

It is to systems of the second class, that is, those in which the gold is dissolved and simultaneously deposited, that most of the many processes and patents which have appeared in the last fifteen years belong. An apparatus which provides for a continuous process that will dissolve the gold from the ore and at the same time deposit it electrolytically on the cathode has many apparent advantages, and has attracted a great number of workers.

The method which has had a more extensive practical trial than any other is that of Pelatan and Clerici. In general the decomposition apparatus may be described as consisting of a circular vat 10 feet in diameter and 8 feet deep. The bottom is lined with copper on which rests a layer of mercury about 1 inch deep, and which together with the copper form the cathode. A strong central agitator carrying blades of wrought iron forms the anode.

The finely-crushed ore is mixed with a solution of common salt and potassium cyanide in the proportion of five of the ore to three of the solution. This pulp is run into the decomposing vat and agitated while an electric current is passing through for from twelve to twenty hours. On an average for every ton of ore treated are consumed from 2 to 2½ pounds of cyanide and 6 pounds of salt, while from 3 to 8 ounces of mercury are lost. Although a low current density is employed, owing to the small amount of solution or electrolyte present, the voltage across the terminals runs from 5 to 14. In practice this system is really a combination of pan amalgamation, which takes care of the coarse gold, and solution of the fine gold in cyanide with electrical precipitation. Although a plant was erected at the De Lemar mill in Idaho, and at one or two other places, for some reason they have not been successful, and have been changed so as to work on other systems.

A modification of this idea which has been employed somewhat in South Africa, and more lately in the United States, is that of Rieken. In this apparatus the sloping slides of the vats as well as the bottom are of copper. A constant stream of mercury is caused to flow over these plates, the circulation being maintained by a pump. The electrolyte is again potassium cyanide to which has been added common salt; the presence of the latter increases the conductivity of the pulp and during electrolysis furnishes the oxygen necessary for the production of the soluble potassium aurous cyanide. Several units of this system are operated at the works of the Telluride Reduction Co., Colorado City, with, it is claimed, great success. The refractory ore is first given a dead roast and then put through the above apparatus.

The only other method for applying this idea which need be noted here is the so-called Aurex-sluice system, based on a United

States patent issued to Motz in 1900. This process aims at economizing time by making the operation continuous, and at an economy of power by moving the ore largely by gravity. The apparatus consists in a long trough having a bottom composed of amalgamated copper plates arranged in steps; these also form the cathodes. Suspended above these plates are the lead anodes curved so as to bring the surface nearest the cathodes at the point where the movement of the ore is the most rapid. Although the process has been given one or two trials in America it does not seem to have been successful.

One great disadvantage common to all processes of this type is the difficulty encountered in the constant and uniform movement of the great masses of ore which it is necessary to treat. Even though the ore be a comparatively rich one and contain ½ to 1 ounce of gold per ton, the output of pieces of apparatus such as have been described is necessarily a small one.

With the possible exception of a process patented by W. L. Brown in 1897, all of the many methods proposed for the direct electrolytic extraction of gold from its ores provide for first dissolving the gold or compounds of gold in the electrolyte, and subsequently precipitating the precious metal upon the cathode. It is true that some processes for amalgamating free gold provide for the constant deposition of sodium on the mercury, thus keeping it "alive," or for preventing it from becoming "sick;" but when the gold is carried by so-called rebellious ores, such as sulphides, arsenides, tellurides, etc., provision is always made for first dissolving the refractory bodies at the anode, or at least in the anode liquor with the subsequent plating out of the gold on the cathode. The electrolyte employed is almost always a solution of potassium cyanide or sodium chloride, or a mixture of both.

While experimenting upon a number of these processes designed to treat rebellious ores with a view to obtaining a method for working some low-grade telluride ores from Cripple Creek, Colorado, an observation was made which may possibly explain in part at least the failure of a number of trials made on similar ores both in America and Australia.

In an experiment designed to determine the effect of chlorine and cyanogen at the moment of liberation at the anode, ore was spread on a piece of platinum foil immersed in a solution of salt

and potassium cyanide. The electrode intended to act as cathode was suspended from above. Through an error the feed wires were crossed and the platinum plate on which rested the ore was made the cathode. Almost immediately after turning on the current a purplish-red color was observed around the plate and subsequently a black cloud was thrown off. Upon removing the ore the gold was found securely plated upon the platinum, while the black cloud, when collected and analyzed, proved to be tellurium. To prove that the anions Cl and CN played no part in the reaction caustic soda was substituted as electrolyte and identical results obtained. Evidently the gold was being recovered by cathodic reduction alone.

The subject was studied further by Mr. W. C. Martin, and it was found that, in general, any method which subjected the telluride to the action of nascent hydrogen in an alkaline solution would effect the reduction; or to put it differently, whenever gold telluride in the presence of alkali came in contact with a metal from which hydrogen was being liberated, tellurium was set free, and metallic gold appearing on the metal. Thus, for example, when powdered telluride is placed upon metallic aluminium and moistened with caustic soda decomposition immediately takes place. The same is true of zinc, although the reaction is much slower. Sodium amalgam breaks up the grains of telluride with great ease. When an electric current is used the reaction seems to be independent of the metal forming the cathode, and to take place in any neutral or alkaline solution.

When a dilute acid was used as an electrolyte a reduction of the gold was effected with the greatest difficulty. Only by employing a very dilute acid and a large current density could any apparent decomposition be obtained.

A possible explanation of the reaction taking place is the following: The hydrogen evolved first unites with the tellurium, forming hydrogen telluride and free gold. In the presence of alkali this compound is immediately broken up with the formation of an alkaline telluride which is easily soluble, and thus removes the tellurium from the sphere of action. This alkaline telluride is in turn easily oxidized with the formation of free alkali and metallic tellurium. In the presence of acids, however, the hydrogen telluride is immediately broken up and the free

tellurium deposited *in situ,* as it were, upon the gold, thus protecting it from further action. This is indicated by the fact that a silver white piece of gold telluride becomes black when placed upon the cathode in an acid electrolyte, and also by the fact that when the amount of active hydrogen is increased by raising the current density, and the activity of the acid decreased by diluting the solution a slight deposition of gold can be obtained.

When the rate of decomposition is rapid the gold in the small pieces of mineral is not evenly deposited, but frequently retains the original shape of the mineral fragment.

Quantitative runs were made on a rather rich sulpho-telluride ore from Cripple Creek, Colorado, using 5 per cent caustic soda as electrolyte, and mercury for the cathode. By maintaining good agitation it was not difficult to obtain an extraction of 93 per cent of the assay value. The presence of finely-divided tellurium in the electrolyte seemed to cause excessive flowering of the mercury and much trouble was experienced from this cause. When lead or other solid metal was used as cathode much gold was lost by the abrasion of the moving ore.

Good results were also obtained by agitating the ore with aluminium shavings in the presence of caustic soda solution, washing out the tellurium, and amalgamating the free gold.

The enormous practical difficulties in the way of using a method of this kind is appreciated when we consider that every minute particle of mineral scattered through the relatively enormous quantity of gangue must be brought into direct contact with the surface, liberating the hydrogen before any reaction will take place. The fact that tellurides of gold are insoluble in potassium cyanide, and so far as electrolytic methods are concerned are effected only by cathodic reduction may explain why many electrolytic processes have promised well when experimenting with rich ores, but have failed when worked upon poor or lean ores. With a rich ore on a small scale it is not difficult to bring a large percentage of the individual particles into direct contact with the active surface and thus get a high extraction, even though the experimenter was ignorant of the reaction by which the values are recovered. In a lean ore, however, on a practical scale each particle of ore is surrounded by such a great quantity of gangue that an amount of agitation sufficient to keep the ore in suspension

and to allow the passage of the electric current is not capable of effecting complete reduction at the cathode or other active surface.

As a result therefore of the fact that in ores of gold the amount of precious mineral is so minute when compared with the quantity of worthless gangue with which it is associated, and to the apparent misunderstanding of at least some of the reaction taking place, the application of electrochemistry to the metallurgy of gold has not been productive of results comparable to its achievements of this branch of science along other lines.

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DISCUSSION.

DR. W. D. BANCROFT: I have seen a statement in the *Mineral Industry*, coming from South Africa, to the effect that they have substituted there largely the Andreoli process, also owned by the Siemens & Halske firm; that is, of lead peroxide anodes and iron cathodes instead of the iron anodes and the lead cathodes. The advantages claimed are the ease of stripping cathodes, and that the lead peroxide anodes do not deteriorate; whereas iron dissolves very rapidly in dilute cyanide. From the same source I obtained some figures which, of course, lay no claim to great accuracy, but that work out for a current efficiency of considerably less than 1 per cent.

PRESIDENT RICHARDS: I have experimented frequently with the precipitation of the gold by the Siemens-Halske process, making careful tests of the amount of gold precipitated and the current used; and the best results which I could get were one quarter of 1 per cent efficiency on the ampères used. However, a few ampères will precipitate a great many hundred dollars, or thousands of dollars' worth in a day, if you have 100 per cent efficiency; so that the fact that the efficiency is only one-quarter of 1 per cent on the ampères does not cut any figure. I believe a plant precipitating $15,000 worth of gold in a month only needs 10 horse-power for precipitation, even at that low efficiency.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1903, President Richards in the Chair.

ELECTROLYTIC COPPER REFINING.[1]

By Wilder D. Bancroft.

In determining the best conditions for the electrolytic refining of copper, we must consider the cost of the power necessary to precipitate a tank-full of copper under different current densities and at different temperatures; the cost of heating the tank; the deterioration of the electrolyte; the interest charge on the copper in the tank; the cost of pumping, and the quality of the copper deposited. Good adherent copper can be obtained at almost any current density, provided the rate of circulation be sufficient. The question of the cost of pumping has not been taken up, and is supposed to remain constant while the conditions are varied. The watt hours necessary to precipitate a gram of copper increase with increasing current density, and decrease with rising temperature. The cost of heating increases with rising temperature, and the interest charge on the copper in the tank decreases with increasing current density. With increasing current density, we have to strike a balance between the increasing power and the decreasing interest charge. With rising temperature, we have to strike a balance between the decreasing cost of power and the increasing cost of heating. The object of this paper is to furnish data bearing on these points Two of my students, Messrs. Schwab and Baum, have therefore determined the relation between voltage, current density and temperature for pure copper plates set a definite distance apart in four solutions. By expressing the voltages in terms of the voltage at 20°, the effect of the distance between the plates is eliminated, and the percentage variations hold for any set of plates in the same solutions. Data have been obtained showing the relations between current efficiency, current density and temperature for pure copper plates in four different solutions. These experiments were necessary because Foerster

[1] For further particulars see Jour. Phys. Chem. 7, 493 (1903).

and Seidel[1] had found a marked falling off of the current efficiency above 50°. These runs also give the degree of neutralization of the acid by copper. Incidentally, some experiments have been made on the effect of iron salts. The cost of heating tanks similar to those used by the Baltimore Copper Co. has been determined, and Messrs. Schwab and Baum have calculated the variation of the cost with varying conditions of temperature and current density for the case of all power costing at the rate of $20 per horse-power year, and for the case in which steam heating costs only one-thirtieth of electrical heating.

Test No. 1.

The object of this test was to determine the variation of voltage with variation of temperature, current density and solution. In commercial copper refining two standard solutions are used, each solution containing 16 per cent copper sulphate crystals. The refineries using the Hayden system make up their electrolyte to contain also 6 per cent sulphuric acid, while the plants operating with the multiple system use a 9 per cent acid solution. It has been claimed that the addition of a small quantity of sodium chloride produces a more coherent form of copper at the higher current densities. Experiments were therefore made with the following solutions:

Solution A.

16 per cent $CuSO_4 5H_2O$ and 9 per cent sulphuric acid.

Solution B.

16 per cent $CuSO_4 5H_2O$ and 6 per cent sulphuric acid.

Solution C.

Solution A + sodium chloride (1 : 2,000,000 of solution).

Solution D.

Solution B + sodium chloride (1 : 2,000,000 of solution).

Pure copper plates, 5 centimeters wide and dipping 10 centimeters into the solution, were used as electrodes, one cathode and two anodes. The plates were held 1 centimeter apart, and arrangements were made for efficient stirring. The four solutions were placed in four beakers, and the measurements made under practi-

[1] Zeit. anorg. Chem. **14**, 138 (1897).

cally the same conditions by means of Weston instruments which had been compared with a standard. The four beakers stood in a large water bath. The results are given in Tables I-II, and refer to measurements made with rising temperature. The voltage readings are in volts; the temperature readings in centigrade degrees. The temperature variations amount to a degree in some cases.

TABLE I

Amp/qdm	A	B	C	D
		20° VOLTAGE RUN		
1.0	0.160	0.173	0.167	0.171
1.5	0.205	0.221	0.211	0.221
2.0	0.244	0.262	0.252	0.267
2.5	0.275	0.299	0.284	0 306
3.0	0.317	0.342	0.322	0.350
3.5	0.354	0.384	0.366	0.396
4.0	0.399	0.424	0.414	0.439
		30° VOLTAGE RUN		
1.0	0.114	0.129	0.127	0.129
1.5	0.165	0.180	0.173	0.181
2.0	0.200	0.223	0.211	0.224
2.5	0.237	0.262	0.247	0.264
3.0	0.264	0.292	0.274	0 299
3.5	0.298	0.334	0.306	0.335
4.0	0.330	0.365	0.339	0.374
		40° VOLTAGE RUN		
1.0	0.088	0.099	0.098	0.103
1.5	0.130	0.146	0.142	0.149
2.0	0.165	0.188	0.178	0.190
2.5	0.197	0.223	0.211	0.226
3.0	0.225	0.255	0.238	0.259
3.5	0.248	0.287	0.260	0.288
4.0	0.274	0.314	0.289	0.318
		50° VOLTAGE RUN		
1.0	0.071	0.084	0.081	0.085
1.5	0.105	0.122	0.118	0.123
2.0	0.134	0.157	0.149	0.158
2.5	0.166	0.193	0.181	0.195
3.0	0.192	0.224	0.208	0 226
3.5	0.217	0.254	0.233	0.257
4.0	0.239	0.278	0.245	0.279

TABLE II

Amp/qdm	A	B	C	D
		60° VOLTAGE RUN		
1.0	0.062	0.074	0.067	0 074
1.5	0.088	0.104	0.096	0.104
2.0	0.114	0.136	0.125	0.137
2.5	0.140	0.166	0.153	0.168
3.0	0.166	0.196	0.180	0.199
3.5	0.188	0.223	0.206	0.227
4.0	0.213	0.250	0.229	0 254
		70° VOLTAGE RUN		
1.0	0.055	0.064	0.059	0.066
1.5	0.076	0.092	0.083	0.094
2.0	0.098	0.117	0.106	0.119
2.5	0.120	0.142	0.130	0.147
3.0	0.141	0.171	0.154	0.175
3.5	0.165	0.198	0.177	0.202
4.0	0.185	0.224	0.201	0.228
		80° VOLTAGE RUN		
1.0	0.048	0.058	0.050	0.059
1.5	0.068	0.082	0 071	0.083
2.0	0.086	0.105	0.091	0.107
2.5	0.105	0.129	0.110	0.131
3.0	0.124	0.153	0.133	0.156
3.5	0.142	0.175	0.152	0.180
4.0	0.160	0.199	0.171	0.204
		90° VOLTAGE RUN		
1.0	0.044	0.053	0.045	0.054
1.5	0.061	0.076	0 064	0.078
2.0	0.078	0 097	0.081	0.099
2.5	0.096	0.120	0.099	0.122
3.0	0.112	0.142	0.118	0.144
3.5	0.129	0.164	0.135	0.166
4.0	0.146	0.187	0.153	0.189

The voltage required to obtain a given current density is materially less with the 9 per cent acid solution than with the 6 per cent acid solution. The addition of sodium chloride to the solution increases the voltage at the lower temperatures, while the effect is scarcely noticeable at the higher temperatures.

Test No. 2.

CURRENT EFFICIENCY RUN.

The object of this test was to determine the variations of the current efficiency when operating with the different electrolytic solutions at varying temperatures and different current densities. Heretofore it has been claimed that the current efficiency drops off rapidly when working at temperatures above 50° C. It was to verify the correctness or prove the incorrectness of this claim that this test was made.

The apparatus used in this test was practically the same as was used in the voltage test (Test No. 1), with the addition of a copper voltameter run in series with the four other cells.

The electrolyte for the voltameter was made up as follows:

$CuSO_4$	150 grams.
H_2SO_4	100 grams.
Alcohol	150 grams.
Water to make up 1 liter.	

The electrolytes used for this run were the same as those of the voltage run, viz.: Solutions A, B, C and D. Before starting the run, the electrodes were carefully cleansed by immersing in a solution of nitric acid. They were then washed and further cleaned and brightened by sand-papering. They were once more washed and rinsed with strong alcohol, and dried gently over a Bunsen flame. After this preparation, they were accurately weighed. Two anodes and one cathode were used in each of the four cells; three anodes and two cathodes in the voltameter. All anodes and cathodes were weighed both before and after each run. In Table III are given the current efficiencies for the four solutions at four temperatures and four current densities. The runs were so timed that the quantity of electricity passing through the solutions was approximately 3 ampère hours, the exact value being determined from the voltameter reading. In Table IV is given the ratio of the anode loss to the cathode gain for the same solutions under the same circumstances.

TABLE III—CURRENT EFFICIENCY RUN

Temp.	1.0 Amp/qdm	2.0 Amp/qdm	3.0 Amp/qdm	4 0 Amp/qdm
		SOLUTION A		
20°	0.9990	0.9997	0.9998	0.9986
50	0.9958	1.0038*	0.9990	1.0000
70	0.9691	0.9962	1.0088*	0.9973
90	0.9033	0.9579	0.9664	0.9821
		SOLUTION B		
20	0.9997	1.0000	0.9994	0.9951
50	0.9985	1.0037*	0.9990	0.9997
70	0.9682	1.0000	1.0094*	1.0031*
90	0.9121	0.9642	0.9609	0.9917
		SOLUTION C		
20	0.9998	0.9995	0.9994	0.9947
50	0.9953	1.0030*	0.9940	1.0000
70	0.9704	0.9951	1.0088	1.0016*
90	0.9045	0.9623	0.9610	0.9820
		SOLUTION D		
20	0.9990	0.9996	0.9991	0.9963
50	0.9990	1.0035*	0.9989	0.9998
70	0.9700	0.9773	1.0043*	0.9990
90	0.9110	0.9629	0.9641	0.9930

TABLE IV—ANODE LOSS/CATHODE GAIN

Temp.	1.0 Amp/qdm	2.0 Amp/qdm	3.0 Amp/qdm	4.0 Amp/qdm
		SOLUTION A		
20°	1.016	1.010	1.012	1.011
50	1.054	1.023	1.011	1.019
70	1.071	1.055	1.027	1.018
90	1.246	1.116	1.106	1.093
		SOLUTION B		
20	1.016	1.008	1.013	1.015
50	1.041	1.022	1.024	1.020
70	1.086	1.045	1.029	1.024
90	1.203	1.108	1.116	1.076

TABLE IV—(*continued*).

Temp.	1.0 Amp/qdm	2.0 Amp/qdm	3.0 Amp/qdm	4.0 Amp/qdm
		SOLUTION C		
20	1.011	1.008	1.014	1.020
50	1.058	1.252	1.026	1.018
70	1.094	1.055	1.028	1.018
90	1.243	1.115	1.115	1.087
		SOLUTION D		
20	1.014	1.013	1.013	1.015
50	1.040	1.021	1.026	1.019
70	1.086	1.046	1.027	1.018
90	1.207	1.114	1.107	1.075

From Table III it will be seen that the current efficiencies for temperatures below 70° C fall off but very little, and are practically 100 per cent. Even at a temperature of 90° C and a high current density of 4 amp/qdm, the efficiency runs as high as 98 per cent and 99 per cent for the 9 per cent and 6 per cent solutions, respectively, while a current density of 1 amp/qdm gives an efficiency of 90 per cent and 91 per cent.[1] Between 50 and 70 degrees, the efficiency in some cases runs a trifle above 100 per cent. This is no doubt due to the formation of cuprous sulphate in small quantities in the electrolyte. In this salt, copper having a valency of unity, twice as much will be precipitated as from the solutions of cupric salts. This reduction seems to take place most readily at the higher current densities, which probably accounts for the high current efficiencies obtained at the upper limits of temperature.

The deterioration of solution is proportional to the ratio of anode loss to cathode gain, since pure copper plates were used and there was no sediment or copper scrap on the bottom of the beakers. The solution deteriorates more rapidly at the higher temperatures and at the lower current densities. This deterioration of solution probably more than offsets the advantage of decrease in voltage which the higher temperatures give, but only

[1] While this result is apparently in flat contradiction with that of Foerster and Seidel, this is not really the case. These authors find 47 per cent efficiency with 0.3 amp/qdm and 83 per cent efficiency with 1.0 amp/qdm at 100° while we find, at 90°, 91 per cent efficiency with 1.0 amp/qdm and 99 per cent efficiency with 4.0 amp/qdm. The highest current density of Foerster and Seidel is our lowest. Since no refinery in this country runs at as low a current density as 1.0 amp/qdm except the Calumet and Hecla, the conclusions of Foerster and Seidel are not applicable to American practice.

when operating at the lower current densities. The ratio of anode loss to cathode gain, when operating at 70° C and 4 amp/qdm, is hardly any higher than this ratio for operating temperatures between 20° and 50°.

From the data in Tables I-III it is possible to calculate the watt hours per gram of copper for the different solutions under the different conditions, the ratio of the watt hours at x° to those at 20° and the ratio of the voltages at x° to those at 20°. This has been done, and the results are given in Tables V-VIII.

TABLE V—SOLUTION A

Temp.	Amp/qdm	Voltage x° / Voltage 20°	Watt hours per g Cu	Watt hours x° / Watt hours 20°
20°	1.0	1.000	0.135	1.000
50	1.0	0.446	0.060	0.445
70	1.0	0.340	0.046	0.341
90	1.0	0.026	0.039	0.289
20	2.0	1.000	0.206	1.000
50	2.0	0.548	0.112	0.544
70	2.0	0.395	0.082	0.398
90	2.0	0.312	0.067	0.325
20	3.0	1.000	0.268	1.000
50	3.0	0.600	0.161	0.600
70	3.0	0.441	0.118	0.440
90	3.0	0.347	0.095	0.354
20	4.0	1.000	0.337	1.000
50	4.0	0.605	0.204	0.605
70	4.0	0.454	0.153	0.454
90	4.0	0.362	0.124	0.368

TABLE VI—SOLUTION B

Temp.	Amp/qdm	Voltage x° / Voltage 20°	Watt hours per g Cu	Watt hours x° / Watt hours 20°
20°	1.0	1.000	0.144	1.000
50	1.0	0.500	0.072	0.500
70	1.0	0.376	0.056	0.389
90	1.0	0.306	0.048	0.333
20	2.0	1.000	0.220	1.000
50	2.0	0.607	0.134	0.608
70	2.0	0.450	0.099	0.450
90	2.0	0.370	0.084	0.383
20	3.0	1.000	0.287	1.000
50	3.0	0.655	0.188	0.655
70	3.0	0.505	0.144	0.502
90	3.0	0.415	0.124	0.432
20	4.0	1.000	0.358	1.000
50	4.0	0.659	0.235	0.656
70	4.0	0.520	0.186	0.520
90	4.0	0.440	0.159	0.444

TABLE VII—SOLUTION C

Temp.	Amp/qdm	Voltage x° / Voltage 20°	Watt hours per g Cu	Watt hours x° / Watt hours 20°
20°	1.0	1.000	0.141	1.000
50	1.0	0.490	0.069	0.490
70	1.0	0.353	0.052	0.369
90	1.0	0.270	0.042	0.298
20	2.0	1.000	0.212	1.000
50	2.0	0.600	0.127	0.595
70	2.0	0.416	0.088	0.413
90	2.0	0.325	0.072	0.338
20	3.0	1.000	0.273	1.000
50	3.0	0.649	0.177	0.647
70	3.0	0.477	0.130	0.475
90	3.0	0.366	0.104	0.380
20	4.0	1.000	0.357	1.000
50	4.0	0.650	0.216	0.648
70	4.0	0.481	0.169	0.474
90	4.0	0.371	0.133	0.372

TABLE VIII—SOLUTION D

Temp.	Amp/qdm	Voltage x° / Voltage 20°	Watt hours per g Cu	Watt hours x° / Watt hours 20°
20°	1.0	1.000	0.145	1.000
50	1.0	0.496	0.073	0.503
70	1.0	0.380	0.057	0.392
90	1.0	0.316	0.050	0.344
20	2.0	1.000	0.226	1.000
50	2.0	0.600	0.135	0.600
70	2.0	0.453	0.102	0.450
90	2.0	0.370	0.087	0.385
20	3.0	1.000	0.296	1.000
50	3.0	0.649	0.193	0.652
70	3.0	0.500	0.149	0.504
90	3.0	0.409	0.127	0.429
20	4.0	1.000	0.372	1.000
50	4.0	0.649	0.241	0.647
70	4.0	0.522	0.193	0.519
90	4.0	0.430	0.161	0.432

EFFECT OF IRON IN ELECTROLYTE.

Frequent statements have been made that the presence of iron in the electrolytic solutions cuts down the current efficiency. To investigate this the following solutions were prepared:

Solution (a), $CuSO_4.5H_2O$ ..... 16 per cent
H_2SO_4 ..... 5 per cent

Solution (b), $FeSO_4.7H_2O$ . . . . . 18.4 per cent
H_2SO_4 . . . . . 6 per cent
3 cc HNO_3 per liter of solution (b).

These stock solutions were mixed in varying proportions:

9 volumes (a), 1 volume (b) . . . . (Solution 1)
8 " " 2 " " . . . . (Solution 2)
7 " " 3 " " . . . . (Solution 3)
6 " " 4 " " . . . . (Solution 4)

These solutions were electrolyzed between weighed copper electrodes at a temperature of 45° C and a current density of 2 amp/qdm, with a voltameter in series. The same apparatus was used as in the current-efficiency run. The results obtained show that there is no falling off in the current efficiency. Thinking that perhaps enough nitric acid had not been added to change a sufficient quantity of ferrous iron to the ferric condition, another solution of iron was made up, to contain 20 cc nitric acid per liter, instead of 3 cc. The run was continued, using this new solution. The results obtained tallied with the first, showing no decrease in current efficiency. After the test the precipitate on the cathode was dissolved in nitric acid, and the solution was tested for iron. None was found, thus demonstrating that iron was not precipitated from the solution.

The results of this run are given in Table IX.

TABLE IX—EFFECT OF IRON IN ELECTROLYTE.

Temp. 20°, Current density 2.0 amp/qdm.

Sol.	Current Efficiency	Anode / Cathode	Sol.	Current Efficiency	Anode / Cathode
	3cc HNO_3 /liter (b)			20cc HNO_3 /liter (b)	
1	0.9986	1.032	1	0.9980	1.035
2	0.9996	1.025	2	0.9997	1.035
3	1.0000	1.028	3	0.9996	1.035
4	0.9988	1.025	4	0.9978	1.040
5	1.0000	1.011	5	1.0000	1.019

Test No. 3.

RADIATION RUN.

One of the important items in electrolytic copper refining is the cost of maintaining the electrolytes in the vats at operating temperature. To form some idea of the relative costs of operating at various temperatures was the object of this test.

Of course, it was impossible to make a radiation run with a vat of such a size as is used in an electrolytic copper-refining plant, but an effort was made to duplicate commercial conditions on a small scale.

The vats in a plant using the Hayden system are 9 feet long, 2 feet wide and 2½ feet deep, and are filled with copper plates, ½ inch apart. Accordingly, there was constructed a small tank out of ½-inch stock, with inside dimensions of 9 x 2 x 2½ inches, and filled it with copper plates ½ inch apart. The joints of the tank, as well as the inside, were lined with tar, thus effectually preventing leaks.*

As a means of heating up the tank, a platinum coil was placed on the bottom, and connections brought out to binding posts on the sides of the tank. Next the tank was filled up with electrolytic solution (Solution A), and its temperature brought up to near the boiling point by passing an alternating current through the platinum coil. The object of using an alternating current was to prevent precipitation of copper on the platinum coil, which would thereby increase its conductivity and cut down the heating power when working with the current for which the coil was designed. When the solution had reached a temperature of about 95° C, the current was turned off and the run started.

A standard thermometer was placed in the electrolyte, and readings of its temperature taken at varying intervals of time, until the temperature had dropped to about 40° C. Two radiation runs of this sort were made—the first with the tank uncovered, and the second with a cover over the top. These measurements are given in Table X, the time being given in minutes.

* The external surface of a commercial tank is approximately one hundred times the external surface of the small tank.

TABLE X—RADIATION RUN

Room Temperature 24.8°.

TANK COVERED				TANK UNCOVERED			
Temp.	Time	Temp.	Time	Temp.	Time	Temp.	Time
96.1°	0.0	78.7°	23.0	94.5°	0.0	69.8°	14.5
95.0	0.5	76.0	27.5	92.2	0.5	67.7	16.5
94.2	1.0	73.1	32.5	90.7	1.0	65.9	18.5
93.6	1.5	70.5	37.5	88.1	2.0	63.7	21.0
93.1	2.0	68.2	42.5	85.6	3.0	61.5	24.0
92.2	3.0	66.0	47.5	83.5	4.0	59.0	27.5
91.5	4.0	63.9	52.5	81.4	5.0	56.8	31.0
90.8	5.0	61.9	57.5	79.6	6.0	55.0	34.0
89.7	6.5	59.9	62.5	77.2	7.5	52.4	40.0
88.6	8.0	56.5	72.5	75.2	9.0	48.2	50.0
87.2	10.0	53.3	82.5	73.2	10.5	44.7	60.0
85.7	12.0	50.6	92.5	71.4	13.0		
84.2	14.0	48.2	102.5				
82.4	17.0	46.0	112.5				
80.5	20.0	44.1	122.5				

The tank was again heated up to 90° C, and the current so adjusted that the temperature of the solution was maintained constant. A wattmeter and ammeter were placed in series with the tank. In order to make accurate readings of the power required to overcome radiation at 90° C, the potential side of the wattmeter was stepped up to ten times the pressure at the terminals of the vat by means of a ten to one transformer. This reduces the error of reading to practically a negligeable amount, since the actual watts required will be only one-tenth of the wattmeter reading. The power required to overcome radiation at 90° was determined both for covered and uncovered tanks.

As would naturally be expected, radiation takes place much more rapidly from the uncovered tank. The power required to overcome radiation at any particular temperature is directly proportional to the slope of the radiation curve at that temperature. Hence, to find the number of watts at any particular temperature necessary to overcome the radiation, one simply multiplies the watts required at 90 degrees by the ratio of the tangent to the curve at the particular temperature and the tangent at 90°. The power required at several different temperatures was computed for both covered and uncovered tanks, and the data are given in Table XI.

TABLE XI—CONSTANT TEMPERATURE—POWER DATA.

TANK COVERED				TANK UNCOVERED			
Temp.	Watts	Temp.	Watts	Temp.	Watts	Temp.	Watts
90°	44.0	65°	25.2	90°	145.0	65°	42.0
85	40.1	60	21.7	85	118.0	60	34.4
80	36.6	55	18.8	80	90.4	55	26.4
75	33.5	50	14.5	75	67.3	50	20.6
70	28.8			70	50.6		

Since the radiation of any two similar bodies is directly proportional to the area of their radiating surfaces, these values of power as determined for the small tank can be easily translated to figures for a tank of commercial size by multiplying by 100. Of course, it is not to be expected that these results will be entirely accurate, as the temperature gradient for the small tank enters in to a far greater extent than for the larger commercial tanks. But the results obtained can be safely said to be accurate to within 10 or 20 per cent, since in a subsequent run on a larger tank the results checked very closely.

The further discussion will be confined entirely to covered tanks, as it is obvious that the most efficient results can be obtained from their use. At 50° the uncovered tank needs 42 per cent more power, and 75 per cent more power at 70°.

COMMERCIAL TEST.

In this test an attempt was made to duplicate commercial conditions in the precipitation of electrolytic copper. Through the courtesy of the Baltimore Copper Co., several hundred pounds of their commercial anode plates were obtained. These plates were 24¼ inches long, 11 inches wide and ¼ inch thick. They were cut in two, thus giving anode plates 11 x 12⅛ inches.

The tank used was built of ¾-inch stock, of inside dimensions 13 x 13 x 13 inches, and lined with tar to make it water-tight. A piece of sheet glass was fitted in the bottom, covering it completely, for the purpose of preventing the slimes from sticking to the tar lining. Small rectangular pieces of wood, having ¼-inch grooves cut their entire length, were used as distance pieces, allowing the plates to be stacked ½ inch apart.

Ten commercial anode plates were used, and a thin sheet of copper composed the end cathode. The method of arranging the plates was according to the Hayden system. The plates did not rest upon the bottom of the tank, but were suspended about an inch therefrom. The tops of the plates were likewise an inch from the top of the tank. The tank was then filled with solution, covering the plates completely.

The composition of this electrolyte was:

$CuSO_4 . 5H_2O$ ..... 16 per cent
H_2SO_4 ..... 9 per cent
Water to make 1 liter.

As a means of maintaining the tank at a temperature of 45° C., a ½-inch glass tube was used, one end of which extended to within an inch of the tank's bottom, while the other end extended down only an inch below the top of the tank. The tube was heated by means of a Bunsen burner, which not only kept the electrolyte up to the required temperature, but provided a good circulation from the bottom of one end of the tank to the top of the other. Thinking that this circulation might not be adequate, a stirring rod, operated by a small motor, was also provided.

Current to the cell was supplied during the day by a small direct-current generator, and at night by a battery of storage cells. In the circuit was inserted an ammeter, ampère-hour meter and a recording ammeter, while a voltmeter was placed across the terminals of the cell. The current was adjusted to 20 ampères, which gave a current density a little over 2 amp/qdm. The voltage across the terminals of the tank rose from 1.75 volts, at the beginning of the run, to 2.10 volts, three and a half days later. This was due to the deterioration of the solution; that is, to the neutralization of the acid.

After a run of about two hundred hours, it was discovered that some of the plates had become short-circuited by a growth of copper along the bottom of the plates. In stacking up the plates, to raise them from the bottom of the tank, we used a strip of wood upon which the distance pieces rested, thus giving a liquid joint extending clear across the tank. In the actual Hayden system, the grooves in the distance pieces are not cut all the way to the bottom, thus holding up the plates and doing away with this

liquid joint. The short-circuiting in our case was caused by a growth of copper along this joint. This occurrence rendered all readings of power consumed incorrect, and therefore useless as data. The run was here concluded, the slimes washed from the plates and collected from the tank, washed carefully and dried. In all, about 90 grams were taken out. The slimes were analyzed, and found to contain 41 per cent silver and quite an appreciable amount of silica, which probably came from the linings of the blast furnace. The silver in the slimes was recovered by dissolving them in nitric acid, evaporating to dryness and taking up the residue in a dilute solution of sulphuric acid, then precipitating from this solution by means of copper strips.

As the current efficiency could not be computed from the results of this run, an extra determination was made with a commercial anode, using the current-efficiency apparatus previously described. The results obtained are tabulated below:

$$\frac{\text{Anode loss}}{\text{Cathode gain}} = 1.0330$$

$$\text{Current efficiency} = 0.9915$$

This run was made at 45° C and a current density of 2 amp/qdm. From the current efficiency obtained, it is clear that the impurities in the anode do not cut down the current efficiency to any great extent. The current efficiency of commercial tanks does not reach this high figure, probably due to leakage of the current through the slimes on the bottom.

The color of the solution at the end of the commercial run was a decided green, due to the presence of ferrous arsenate in solution.

Calculations for Cost of Refining.

Basis.—One tank, inside dimensions 2 x 2½ x 9 feet. Outside dimensions taken as 29 x 34 x 112 inches, giving a radiating surface of 16,000 square inches. Ratio of radiating surface of small experimental tank to commercial tank is about 1 to 100.

Solution D.

The basis for the following figures on the cost of production are as follows:

One tank, containing 130 electrodes of two plates each.
Weight of copper per tank = 5,700 pounds.
Value of copper per tank = $800.
Cost of power = $20 per H. P. year.
Plant temperature = 20° C.

The calculation is on the basis that the heating of the electrolyte is done by means of the electric current. In such cases, where the cost of heating the solution is greater than the cost of precipitating the copper, we have taken as the figures of cost the former, and *vice versa,* since, in precipitating the copper, the energy is consumed simply in overcoming the resistance of the electrolyte, and thereby heating it.

1 pound = 453.6 grams.
5,700 pounds = 2,684,000 grams copper = N.

Area of electrodes = 22 x 23 inches = 506 square inches = 32.65 qdm. Current density of 1 amp/qdm = 32.65 amp, which will deposit 32.65 × 1.181 × 24 × 130 = 120,500 grams copper per day per tank. Therefore, it requires 2,684,000/120,500 = 22.3 days, or 535 hours, to precipitate one tank full of copper, operating at a current density of 1 amp/qdm. Interest on one tank of copper (value $800) for 22.3 days at 6 per cent = $2.975.

At 2 amp/qdm interest = 2.975 % 2 = $1.487.
At 3 amp/qdm interest = 2.975 % 3 = $0.992.
At 4 amp/qdm interest = 2.975 % 4 = $0.744.

At 20° C, 1 amp/qdm it requires 0.145 × N = 390,000 watt hours to precipitate one tank of copper.

At $20 per H. P. year, 1 K. W. hour costs $0.00306.
Therefore, 390 K. W. hours costs $1.195.
Therefore, total cost to deposit one tank of copper at 20° C and 1 amp/qdm = $1.195 + $2.975 = $4.170.

1 amp/qdm 50° C.

Cost to deposit = $1.195 × 0.503 = $0.601.
Required to heat = 1.48 × 22.3 × 24 = 793 K. W. hours.
Cost to heat = 793 × $.00306 = $2.425.
Interest = $2.975.
Total = $2.425 + $2.975 = $5.400.

1 amp/qdm 70° C.

Cost to deposit = \$1.195 × 0.392 = \$0.468.
Cost to heat = 2.9 × 22.3 × 24 × 0.00306 = \$4.750.
Interest = \$2.975.
Total cost = \$4.755 + \$2.975 = \$7.730.

1 amp/qdm 90° C.

Cost to deposit = \$1.195 × 0.344 = \$0.411.
Cost to heat = 4.4 × 22.3 × 24 × 0.00306 = \$7.205.
Interest = \$2.975.
Total cost = \$7.205 + \$2.975 = \$10.180.

In a similar manner the costs for other current densities were computed, and the results are shown in Table XII.

TABLE XII—COST OF REFINING TANK OF COPPER.

Amp/qdm	Temp.	K. W. hours to Deposit	Cost to Deposit	K. W. hours to Heat	Cost to Heat	Interest on Copper	Total Cost
1.0	20°	390	\$1.195	000	\$0.00	\$2.975	\$4.17
1.0	50	196	0.601	793	2.425	2.975	5.40
1.0	70	153	0.468	1550	4.755	2.975	7.73
1.0	90	134	0.411	2360	7.205	2.975	10.18
2.0	20	608	1.86	000	0.00	1.487	3.35
2.0	50	362	1.11	396	1.21	1.487	2.70
2.0	70	274	0.84	775	2.38	1.487	3.87
2.0	90	233	0.71	1180	3.60	1.487	5.09
3.0	20	795	2.43	000	0.00	0.99	3.42
3.0	50	519	1.59	264	0.81	0.99	2.58
3.0	70	400	1.22	517	1.58	0.99	2.57
3.0	90	341	1.04	787	2.40	0.99	3.39
4.0	20	1000	3.06	000	0.00	0.74	3.80
4.0	50	647	1.98	198	0.61	0.74	2.72
4.0	70	519	1.59	388	1.19	0.74	2.33
4.0	90	433	1.33	590	1.80	0.74	2.54

While these figures are based on experiments with the series system, it is probable that the conclusions to be drawn would apply equally well to the multiple system. The kilowatt hours per kilogram of copper will be larger in a multiple tank, owing to the greater distance between plates. The radiation losses are probably also greater, owing to the tanks being relatively wider. Otherwise there is little difference, since the extra interest charge in the multiple system, owing to the use of thick anodes, is offset by the possibility of removing the cathodes before the end of the run, which cannot be done in the series system.

Exception may be taken to these estimates of cost on the ground

that, in practice, the solutions are heated by steam coils, and that this costs less than electrical heating. To meet this objection, the results have been calculated on the basis of electrical power at $20 per horse-power year, and steam heating at one-thirtieth the price of electrical heating. So far as can be learned, this probably constitutes a lower limit, so that the commercial results would be between the two, since steam heating would not be used if it cost more than electrical heating. The data for the two calculations are given in Table XIII, and show cost per ton of copper instead of per tank.

TABLE XIII—COST PER TON OF COPPER.

Amp/qdm	Temp.	Cost 20—20	Cost 20—20/30
1	20°	$1.46	$1.46
1	50	1.89	1.28
1	70	2.78	1.25
1	90	3.57	1.27
2	20	1.17	1.17
2	50	0.95	0.91
2	70	1.36	0.83
2	90	1.79	0.80
3	20	1.20	1.20
3	50	0.91	0.91
3	70	0.90	0.78
3	90	1.19	0.72
4	20	1.33	1.33
4	50	0.95	0.95
4	70	0.82	0.82
4	90	0.89	0.89

It must be kept in mind that these estimated costs do not include the cost of labor, and are based on the assumption of 100 per cent current efficiency. The cost of labor will vary from one plant to another, but is known to each superintendent. Since the number of men employed does not vary with the current density, the cost of labor per ton of copper will be less the higher the current density. The correction for the actual current efficiency is easy to apply when one has the data, and will not affect the general results, because the current efficiency is practically independent of the temperature and current density at temperatures below 90° and within the range of current density considered. The question of the deterioration of the electrolyte need not be

considered, because the amount of deterioration is also practically independent of the temperature and current density at temperatures below 90°.

Conclusion.

Summing up the results obtained for the different runs, it is now possible to draw conclusions as to what are the most financially economical conditions under which to refine copper electrolytically.

Two sets of curves were plotted, one showing the relation between the cost to precipitate a ton of copper and the operating temperature, the second set showing the relation between the cost to precipitate a ton of copper and the operating current density. From these curves, which are not reproduced in this paper, it is evident that to operate at a temperature of 90° and a low current density is entirely out of the question, not only on account of the cost of power to heat the solution and precipitate the copper, but also on account of the deterioration of solution, which takes place very rapidly under these conditions. At this high temperature and the higher current densities, the cost rapidly approaches a minimum, but here also the deterioration probably more than offsets the advantage of reduced cost of power. To operate at 20° C is not so costly as would seem at first thought. The cost is maximum at the lowest and the highest current densities, reaching a minimum between 2¼ and 2½ amp/qdm.

At 50° it would not be economical to operate at 1 amp/qdm, but the cost drops off very rapidly between 1 and 2 ampères. At the higher current densities the cost fluctuates but very little, reaching a minimum at about 2½ amp/qdm.

The results at 70° seem the most satisfactory, and it is at this temperature that we shall get the best results. Although the cost runs very high at this temperature for a current density of 1 amp/qdm, it begins to drop off very rapidly as the current density increases, until it assumes a practically constant value at the higher current densities. Between 3.5 and 3.75 amp/qdm would be the best current density for obtaining economical results, for at this density no extra power would be required to heat the solution. Operating at this current density, and with the *tanks covered,* the current alone would be sufficient to heat the electro-

lyte to over 80°. In order to secure a good circulation, essential for a good deposit with high current densities, the present method of pumping could be retained. If the gutters leading to and from the pump were properly insulated, the solution would not drop below 70° before returning to the tanks. Moreover, running at this high current density, there would be a considerable saving in the first cost of the plant, inasmuch as fewer tanks are needed for the precipitation of a given amount of copper in a given time.

The lower the cost of heating, the greater the advantage of a high temperature. Lowering the rate of interest decreases the advantage of a high current density. With covered tanks, it will be possible for men to work in the tank room even with the electrolyte at 70°. It has been suggested by various people that covering the tanks would interfere with detecting short circuits, but this point seems not to be well taken. If the covers are so arranged that they will swing or lift open easily, the only difference will be the slight extra time necessary to remove the covers.

If we compare the cost of working under so-called standard conditions of open tanks, a current density of 14 amp/sq ft and a temperature of 50° with the cost of working with covered tanks at 70° and a current density of 3.5 amp/qdm (31.5 amp/sq ft), the saving by the latter method will be very close to a dollar a ton of refined copper when all power is figured at $20 per horse-power year.

Therefore, in order to operate a plant most economically, copper should be refined electrolytically under these conditions:

(1) Covered tanks
(2) Current density 3.5 amp/qdm
(3) Temperature 70°

Cornell University.

DISCUSSION.

PRES. RICHARDS: We have been quite fortunate in having brought before us this, practically the largest of the electrochemical industries, and in having discussion of Dr. Bancroft's paper from two gentlemen practically engaged at the

largest electrolytical refineries in America. Before opening the paper for general discussion I will read these discussions contributed by Mr. Addicks, Mr. Magnus and by Dr. T. R. Rosebrugh, on Dr. Bancroft's paper.

MR. LAWRENCE ADDICKS: (Communicated and read at the meeting).

Electrolytic refining from the standpoint of economy consists of a very nice balance of a number of conditions. Dr. Bancroft has considered some, but has in turn overlooked others which cause him to arrive at what, in the mind of the writer, are erroneous conclusions. I wish to touch on certain of these points in the order in which they occur in the paper.

At the beginning it is stated that "good adherent copper can be obtained at almost any current density, provided the rate of circulation be sufficient." This is true, but we are limited in circulation to a very small rate: otherwise we have a turbid solution and a cathode which is not only impure but which carries a prohibitive amount of silver. A system where a torrent of circulation carries all slimes rapidly out of the tank to be settled or filtered out in the sump might avoid this, but there is no such system in use and the conclusions reached in the paper are applied to existing plants. Insufficient circulation at once means poor deposition and necessitates frequent renewal of the cathode sheets to maintain the current efficiency and entails a corresponding increase in labor cost. Take the Anaconda and Great Falls plants, for example; the former with a density of 11 ampères per square foot draws copper every 35 days, the latter with 40 ampères every two days. Less than four times the density and but a seventeenth the age. The paper does not claim to consider labor cost, but we *must* consider labor cost to make any such sweeping statements as those at the end.

Table 1 shows clearly the influence of differences of concentration at the electrodes in producing counter e. m. f. As this is more or less affected by the circulation the question may at once be raised as to whether these laboratory results correspond to those obtained in practice. I have compared the results given for 50° C. with figures taken on a large scale and find very satisfactory correspondence. The work on temperature co-efficients is more complete than any I have seen elsewhere and is very inter-

esting. An electrolyte with considerably lower resistance than that used could have been prepared, but this would probably not have altered the relative values.

The idea of covered tanks would be greeted with much hesitation by most refiners. It is hard enough to get thorough inspection with an open tank, let alone a closed one. With very high temperatures they would undoubtedly be warranted, as otherwise the vapor in the air would make work unbearable. Their application to a series tank would be much simpler than to a multiple one with its external connections.

Passing to the calculations of cost we at once meet the question of interest on the metals tied up. Many refineries are not charged with this interest at all, the owner of the copper allowing so many days gratis for refining. This may not be reasonable, but it is commercial and it is commercial conditions we have to meet. But every refinery is charged with interest and depreciation on its own plant and these are not considered at all. These changes would revolutionize the cost tables.

Current density and temperature of electrolyte bear vital relations to the cost of refining. Dr. Bancroft has furnished us with some valuable data, and for some refinery his conclusions are true; but against their application to every plant that can obtain power for $20 a horse-power year, I must protest. By the way, how many of us are getting power for $20? You say move to where we can; but then you bring up the whole question of milling-in-transit freight rates.

Mr. Benjamin Magnus: (Communicated and read at the meeting.)

Having read the advance sheets of Professor Bancroft's paper, on "Electrolytic Copper Refining," I submit the following comments:

Regarding test No. 2 (Current Efficiency Run), my experience has been that the ampère efficiency depends entirely on mechanical conditions. If a tank is kept free of most local short circuits, and the solution line is kept from coming in contact with the ground, you can very easily attain a desirable maximum ampère efficiency in practical refining. By "desirable maximum efficiency" I mean an efficiency which can be obtained by an expenditure of labor which costs less than the gain to be gotten by a higher efficiency.

Where the general efficiency is 95 per cent, I have succeeded in getting it up to 97.5 per cent, but the extra labor was not saved by the extra saving in power.

Page 61 has the statement: "The solution deteriorates more rapidly at the higher temperatures and at the lower current densities."

This I have found true for high temperatures, but not for low current densities. At the Anaconda plant, where we have low current densities, we have been able to use the same electrolyte continuously for many years; but at other plants, where the current density is 60 per cent higher than at Anaconda, they find it necessary to renew some part of their electrolyte quite frequently. At low current densities the oxidation of impurities occurs quite freely, thus keeping the electrolyte from becoming fouled with impurities. On page 69 is the statement: "The slimes were analyzed, and found to contain 41 per cent silver and quite an appreciable amount of silica, which probably came from the linings of the blast furnace." I am inclined to believe that the silica found in the slimes came from a siliceous mould wash which most refineries use to smooth the pitted portions of the anode mould. On page 69 is also the statement that "the color of the solution at the end of the commercial run was a decided green, due to the presence of ferrous arsenate in solution." This statement is questionable, as there is no analysis of solution at the end of the run given, and I am inclined to believe that the green color was due to a solution impoverished of copper. We have never been able to determine presence of ferrous arsenate in our electrolytes. Page 72 has the statement: "Since the number of men employed does not vary with the current density, the cost of labor per ton of copper will be less the higher the current density." In actual practice this is not the case. High current densities cut down the interest on copper tied up and the interest on investment for plant, etc. But, as a matter of fact, the plants having high current densities usually have higher labor costs per ton of copper produced than plants using low current densities. I have in mind two well-known plants which use respectively 10.5 and 40.0 amp per square foot, the one with the higher current density having a labor cost 40 per cent greater than the plant using the lower current density.

In summing up, Professor Bancroft says: "Therefore, in order to operate a plant most economically, copper should be refined electrolytically under these conditions:

"(1) Covered tanks.

"(2) Current density 31.5 amp per square foot.

"(3) Temperature 70°."

Only a casual inspection of a tank room in any practical plant would soon convince a visitor of the objection to covering tanks.

Let us discuss, by way of demonstration, the conditions at the Anaconda refinery. The current density is 10.5 amp per square foot, the temperature of the electrolyte is 100° F and the circulation of the electrolyte is 3 gallons per minute. Under these conditions the chemical action in the tank is 1 per cent greater than the electrolytic action, and the voltage per tank is 0.23 volt. In order to keep the solution constant day by day, the extra copper taken up by the solution, due to the 1 per cent greater chemical action, is taken out by means of a tank which has insoluble anodes. The cost of operating this tank is at least eight times the cost of operating a regular depositing tank. (The voltage being 2.) Most electrolytic plants use exhaust steam for heating the electrolyte, but even if they used live steam, which cost $80 per H. P. year, the cost of heating the electrolyte per ton of copper produced would only be from 16 to 35 cents; and if they raised the temperature of their solution to 70° C and raised the current density to 31.5 amp, the excess chemical action would be so great that to free the electrolyte from copper, by means of tanks having insoluble anodes, would cost so much that the saving of power due to warmer solutions would be more than offset.

Anaconda, Mont.
September 5, 1903.

PROF. T. R. ROSEBRUGH: (Communicated and read at the meeting.)

Taking data from papers by Charles E. Emery in Transactions A. I. E. E., it would appear to be impossible with the prices of 1895 to estimate the total cost of 1 ton of coal consumed in a boiler at a Lake Erie port at less than $2.64, when the coal is good enough to show an evaporation test of 10 pounds of water.

This price includes cost of mining, transportation, delivery, removal of ashes, labor of firemen, interest and depreciation of boilers, and being based on large scale operations would, no doubt, be less than in the case in question. Taking this result we have this comparison:—

1 Kilowatt year	31,536 mega-joules for	$20.00
1 ton of coal (2240 lbs.)	26,000 mega-joules for	2.64
hence—	31,536 mega-joules for	3.20

consequently the assumption made in the paper that the cost of steam heating could be as low as one-thirtieth of electrical heating at the above price of $20, appears not to be justified.

Mr. W. McA. Johnson: Most of my work has been done on the refining of nickel, but the conditions of copper refining are not entirely dissimiliar. This paper of Prof. Bancroft's is of interest, for it gives the views of a college professor on a practical process that was developed solely along practical lines. It is meagre enough, but it fills a want in giving determinations of current efficiency under conditions of American practice. The "radiation test" is quite similar to one I made about eighteen months ago, and led me to predict that in a large covered vat the C^2R loss would alone keep the temperature at 60° C., which I found later to be the case. I also plotted curves for the different variables for nickel as did Prof. Bancroft for copper.

Such curves and tables are valuable if one translates the results freely—not literally—to meet the commercial conditions. The cost of power, $20 per E. H. P. Y. is very low, and I believe Prof. Bancroft would have done better to take $35 as a figure typical of American practice. Other considerations also alter the case. In almost all large refineries the waste heat from the refining furnaces is used to help out the boilers. This might reduce the cost of power by a system of book-keeping, and shows that the figure for cost of power is variable.

I doubt whether the rise of e. m. f. from 0.175 to 0.210V was due entirely to the neutralization of acid by the copper. A test of resistance of electrolyte would show that there were two other partial causes: (1) increased resistance due to slime; (2) concentration changes producing back e. m. f. in slimes. In work in the series system I have done, it was found expedient to test

drops between each pair of plates by a voltmeter. A decreased reading would show incipient sprouting. To prevent sprouting I had recourse to a device which allows use of well for slimes. Two assumptions made by Prof. Bancroft, are, to my mind, unwarranted:

(1) The proportion of scrap is not a linear function of the current density.

(2) The elimination of impurities is also not a linear function of the current density.

For example, at 20 ampères per square foot, we might have 8 per cent of scrap, and at 30 ampères, 16 per cent. If it costs $3 to remove from cathode screen, cast and put back in process 1 ton of scrap, we should have an increased charge of 24 cents, against the 30 ampère process. Such considerations are, perhaps, out of place in a paper written "ex cathedra," but they are commercial consideration that confront the metallurgist.

For an additional research I would commend to Prof. Bancroft the behavior of the impurities in a copper anode, what per cent of each is electrodissolved, what per cent is slimed by the action of copper in slimes, what per cent of the slimes is dissolved by the electrolyte, between what limits can they be present in an electrolyte and still not be deposited, and the electrostatic attraction of the cathode for small particles floating in the electrolyte (which effect is often compounded with electrodeposition). What work I have done along above lines convinces me of the importance of a theoretical investigation of this subject.

Dr. W. D. Bancroft: Mr. Addicks maintains that the use of a high current density is impossible at existing rates of circulation. I quite agree that a current density of 40 ampères per square foot calls for a very high rate of stirring, and I am much interested in the implied statement that a good precipitate of copper is not obtained at Great Falls. I do not believe that this objection holds for current densities in the neighborhood of 30 ampère square feet. The Baltimore Copper Co. are running at 18 ampère square feet, and they are nowhere near the danger limit as regards quality of copper.

If no interest is charged, the position of the minimum cost will be displaced. I am inclined to think that the interest charge appears somewhere if only in determining the number of days

allowed gratis for refining. Of course interest on the plant must always be figured in a complete statement.

Mr. Addicks objects to the basis of $20 per horse-power year. As we were omitting the cost of labor, the interest on the plant, etc., there seemed no object in going through calculations for a large number of power costs. The data are there for anyone who wishes so to do. We took $20 as being a fair standard for electrical power generated from water. This seemed the more reasonable because Haber has stated that power can be obtained at $25, where cheap coal is available. I will point out, however, that the higher the cost of power the greater the advantage of 70° over 50°. The alternative estimate of less than $1 a horse-power year for heating, to which Mr. Rosebrugh objects, was meant to be an extreme and was put in as bearing on the question of using exhaust steam.

Mr. Magnus criticizes our statement in regard to the color of the solution and believes "that the green color is due to a solution impoverished of copper." Since the solution becomes richer in copper during the run, this explanation cannot be accepted. The presence of a ferric salt in a copper solution will give a green color; but it takes a great deal of iron to give the green that we found. The presence of arsenic in the solution was shown analytically by the Marsh test. On making up a solution synthetically which contained arsenite, no green color was observed; but the green appeared when a few drops of nitric acid were added.

The criticism of Mr. Magnus in regard to the increased cost of labor with high current density seems to be answered by Mr. Addicks' statement that a satisfactory deposit is not obtained in the plant referred to. Our experiments show that the deterioration of the solution is not appreciably greater at 70° than at 50°.

Mr. Addicks takes the ground that depreciation of plant has an important bearing on the conditions for refining copper. This I cannot admit. The deterioration of the dynamos for a given voltage and ampèrage will be the same if we double the current per cell and halve the number of cells. Working at the same temperature, the decrease in the number of the cells to deteriorate will more than counterbalance the increased rate of deterioration due to the higher current density. On the other hand, the life of a

cell at 70° will undoubtedly be less than at 50°; but, so far as I know, there are no figures to show what this difference of deterioration would actually amount to.

Mr. Johnson's statement that the change of voltage is due to something beside the change of resistance is disproved by the fact that restoring the original concentration of the electrolyte brought the voltage practically back to the original value. So that it is, in our experiments with copper, almost exclusively a question of the increased resistance.

Mr. Johnson: Was any change made in the slimes?

Mr. Bancroft: Without making any change in the slimes. The slimes had little effect.

We now come to the really vital question of covered tanks versus open ones. Granted that there is a slight disadvantage in regard to inspection, the matter is simply a question of relative cost. At 50° you can save approximately 30 per cent of the total power by covering the cell; at 60° it is approximately 37 per cent. Is that 30 per cent worth saving? That is a question which each company must decide for itself.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1903, President Richards in the Chair.

EFFICIENCY OF THE NICKEL-PLATING TANK.

By Oliver W. Brown.

Although the nickel-plating tank is one of the best-known examples of an electrolytic cell, having been used in practical work for many years, there are certain peculiarities and factors about it which are not understood, and which are of such a nature as to leave considerable room for improvement in the process for electroplating with nickel.

The design of the present nickel-plating solution has been the result of the "cut-and-try" process, and few attempts have been made to give a good scientific explanation of why some solutions give better results than do others. The double nickel-ammonium sulphate electrolytes must be carefully watched during operation to insure satisfactory products, and the plater knows that his success depends upon keeping the solution at a chemical composition having somewhat narrow limits. It is known that a small percentage of certain impurities may ruin the solution, and that the electrolyte must not become appreciably acid or alkaline. It is to counteract such tendencies that his attention is principally directed.

An ideal electroplating cell is one which operates at a current efficiency of 100 per cent, and has a resistance sufficiently low that an electromotive force not exceeding five or six volts may send the proper current through it. A current efficiency of 100 per cent. means that the anode shall corrode at exactly the same rate that the metal is deposited at the cathode, this amount being equal to that calculated from the quantity of current and the electrochemical equivalent of the metal. With a current efficiency of 100 per cent., no change in composition of electrolyte will occur, and the greatest of simplicity in the operation will thereby be attained. That the nickel-plating cell, as at present used, is notably inefficient, when viewed from this standpoint, is apparent. It was for the purpose of determining some of the factors which influence

this efficiency that a study was taken up, the results of which are given herein.

Inasmuch as the discharge potentials and polarization pressures are important factors in the study of the operation of the electrolytic cell, these were taken into account for the purpose of throwing some additional light upon the question. If the nickel-plating cell could be made to operate at a maximum efficiency, the electromotive force required to send a current through would be only that necessary to overcome the resistance of the electrolyte, a condition which is almost completely realized in the copper-plating cell using an acidified copper sulphate solution. In nickel plating, however, there is additional pressure which has to be overcome, amounting in some cases to over two volts. This polarization pressure is produced as a result of the fact that the current efficiency is less than 100 per cent, and is the summation of the values at the anode and at the cathode. To determine the variation of these two values and their summation, measurements of discharge potential at the two electrodes were made in the ordinary manner, employing the auxiliary electrode of the "calomel" type, the electromotive force of which was taken as — .56 volts. It was on this value that the measurements recorded herein are based.

The discharge potentials were measured by means of a specially-designed make-and-break switch, which interrupted the current and instantly thereafter made contact with the normal electrode circuit, in which the pressure to be measured was balanced against a pressure of known value. A galvanometer was used as a zero instrument in balancing these two values.

Measurements were first made upon a slightly acid nickel ammonium sulphate solution, taken from a 30-gallon nickel-plating tank. The ordinary cast nickel anodes were used as electrodes. The area of one side of each electrode exposed to the solution was 0.25 square foot. The area of only one side of the electrodes was taken into account in the calculation of the current density, as they were placed flat against the side of a large battery jar. The electrodes were thoroughly cleaned in acid before placing them in the nickel-plating solution.

The discharge potentials of the electrodes and the polarization electromotive force, at different current densities, are given in Table I:

TABLE I

Time at which measurement was made after starting the current at the given current density.	Ampères per square foot	Electrode tension Volts	Discharge potential in volts		Polarization Volts
			Cathode	Anode	
. . . . .	no current	. .	—0.184	—0.154	. . . .
25 Minutes	1.00	0.8	+0.074	—0 290	—0.388
55 "	1.60	1.1	0.164	—0.339	—0.524
25 "	2.80	1.5	0.202	—0 422	—0.650
20 "	4.40	2.3	0.239	—0.474	—0.730
7 "	5.60	. .	0.245	—0.486	—0.750
100 "	6.40	4.2	0.325	—1.725	—2 089
30 "	10.00	4.7	0.403	—1.650	—2.119

It will be noted that the sum of the cathode and anode discharge potentials given in this table does not quite agree with the polarization value obtained. This is due to the unavoidable experimental error in these determinations.

The results in this table are plotted in Curves I, II and III of Plate I. Curve I shows the change of cathode, and Curve II of the anode discharge potential with the change in current density. The polarization at different current densities is shown in Curve III. The anode and polarization curves make a very sudden bend at about 5.6 to 6.4 amp per square foot, the voltage in each case increasing more than one volt. The cathode curve also shows a slight increase in voltage at this current density.

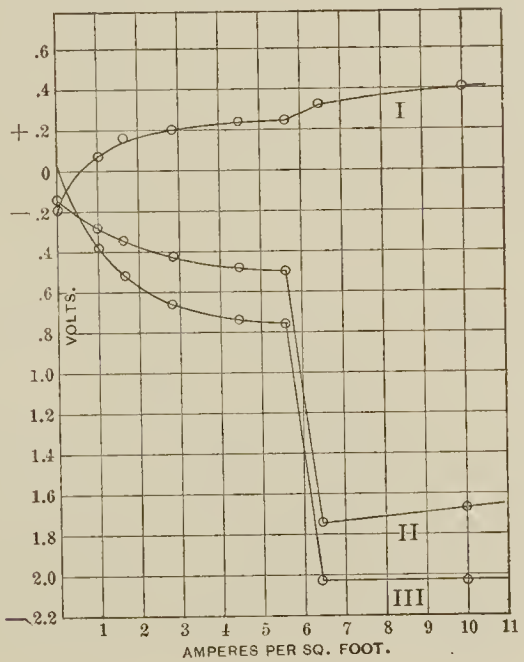

PLATE I.

A high current efficiency is generally supposed to be obtained only when the discharge potential at the electrode is near the single potential of the electrode. If this be true, the current efficiency of corrosion would naturally be expected to decrease to a low value when a current density of about 5.6 amp per square foot is reached. It will be noted from later determinations just how much the efficiency of anode corrosion is lowered by this sudden change in anode potential. A vigorous evolution of gas immediately begins at the anode, when its potential suddenly increases, and the amount of gas evolution increases with the increase in anode potential. No gas is seen at the anode when its potential is — .4 volt. Vigorous stirring of the electrolyte, when the potential first suddenly rises, has no perceptible effect on the potential. In many cases the anode is found to be coated with a thin layer of nickelic oxide when the potential suddenly changes.

In the nickel anode first employed copper was found as an impurity. The nickel dissolved away, leaving the copper on the surface. The presence of the copper, rather than being a detriment, seemed to be advantageous, in allowing a high anode current density to be used without producing a high increase of anode discharge potential. In one set of experiments, where the surface of the anode was found to be covered with a few spots of metallic copper, the anode discharge potential was only — 0.485 volt, and the polarization — 0.816 volt, with a current density of 16.8 amp per square foot. The anode and cathode were removed and thoroughly cleaned with acid, dissolving off the spots of metallic copper. After replacing the electrodes in the solution and passing a current of 14 amp per square foot for twenty minutes, the anode potential had risen to — 0.824 volt and the polarization to 1.964 volts.

A small cell of about 300 cc capacity and two small electrodes, placed about 1.5 inches apart and flat against the sides of the cell, were used in all of the following experiments. The electrodes were weighed on an analytical balance, and the current efficiency of corrosion and deposition determined. The electrolyte used contained 75 grams of nickel ammonium sulphate per liter. This solution had a slightly acid reaction. A fresh sample of electrolyte was used in every experiment, except where noted. The small cast-nickel anodes used were cut from a large cast nickel-

plating anode. Cathodes of pure rolled sheet nickel were used. In some of the experiments these rolled sheets of pure nickel were used as anode. The area of the cathodes in most of the experiments was a little more than 9 square inches (counting one side only). The active surface of the cast anodes, however, was only about 5 square inches.

Table II shows the current efficiency obtained with cast, rolled and electrolytic nickel anodes:

TABLE II.

Nickel anode	Ampère hrs. used	Ampères per square foot		Discharge potential in volts		Current efficiency	
		Anode	Cathode	Anode	Cathode	Corrosion of anode	Dep. of nickel on cathode
Cast, surface gr'nd smooth	0.45	4.12	2.21	—1.834	+0.208	46.29%	75.42%
Cast, surface roughened in acid	0.45	4.12	2.21	—0.44	0.252	91.32	92.06
Rolled, pure . . .	0.45	4.42	4.42	—1.889	0.145	8.47	63.27
Electrolytic . . .	0.45	4.42	4.42	—1.883	0.143	12.65	61.61

These results show that electrolytic nickel anodes corrode very poorly as compared with the cast anodes; also, that pure rolled anodes are no better than the electrolytic. The different efficiencies obtained with cast anodes of smooth and rough surface are of interest. This difference in efficiency between the cast anodes may be due to the difference in current density, caused by the very great increase of *actual* surface of the roughened electrode over the smooth; formation of oxide on the surface of the smooth electrode, or to the electrode assuming a passive state in this experiment. The very high anode potential of the smooth electrodes indicates one of the latter reasons. The cause of this high anode potential will be considered in connection with data given later.

The relative efficiency of the cathode and anode is shown by the results in Table II. The cathode efficiency is affected to a marked degree by the anode efficiency. When the anode efficiency is only about 10 per cent, the cathode efficiency is near 62 per cent, while the cathode efficiency is 92 per cent when the anode efficiency reaches 91.32 per cent. This is an additional reason why rolled or

electrolytic nickel anodes cannot be satisfactorily used in plating. The low anode efficiency reduces the efficiency at the cathode, and and the poor efficiency at both electrodes causes a change in the composition of the electrolyte.

Table III shows the effect of current density on the efficiency of corrosion of a rolled anode:

TABLE III.

Ampère hours used	Ampéres per square foot	Discharge potential of anode	Polarization Volts	Current efficiency	
				Anode corrosion	Nickel deposition
0.10	0.74	—1.829	—2.07	18.64%	64.71%
0.45	2.95	—1.869	—2.10.	19.43	62.79
0.45	4.42	—1.889	—2.143	8.47	63.27

A very poor efficiency at the anode is obtained even with a current density as low as 0.74 amp per square foot. When rolled anodes are used, the corrosion increases slowly as a larger number of coulombs are passed through the solution, while the cathode efficiency decreases.

When the anode corrosion is as low as 19 per cent, the cathode efficiency is as high as 62 per cent. This means that the electrolyte becomes more acid as the number of coulombs passed through the solution increases. The acidity of the solution naturally decreases the amount of metal precipitated at the cathode, and increases the rate of corrosion of the anode. This is shown in Table IV:

TABLE IV.*

Ampère hours	Ampères per square foot	Anode potential	Polarization	Current efficiency	
				Anode	Cathode
0.45	4.42	—1.889	2.050	8.47%	63.27%
0.75	4.42	—1.820	2.052	12.28	51.14
1.531	4.57	—1.858	2 003	15.72	37 88
3.01	3.17	—1.883	2.028	27.08	33.18

From Table IV we see that the polarization and the anode potential change very little with increase in acidity.

* The electrodes were removed from the solution at intervals, weighed, replaced in the electrolyte, and the electrolysis continued.

The ampère hours and efficiencies of Table IV are plotted in Curves I and II of Plate II.

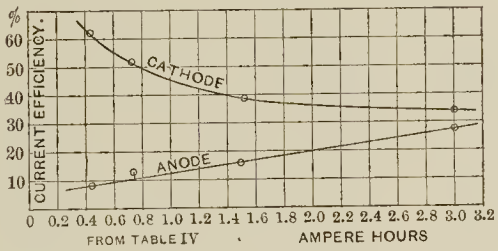

PLATE II.

Table V shows the influence of current density on the corrosion of a cast anode:

TABLE V.

Ampère hours used	Ampères per square foot		Current efficiency		Anode Voltage
	Anode	Cathode	Anode	Cathode	
0.40	7.25	4.42	62.93%	93.51%	—1.87
0.45	5.50	2.95	72.92	90.02	—1.60
0.45	4.12	2.21	91.32	92.06	—0.44
0.40	3.52	2.00	92.17	91.65	—0.30

The efficiency of corrosion of the anode is plotted with the current density in Curve I of Plate III. It is seen that the anode efficiency decreases quite rapidly with increase in current density.

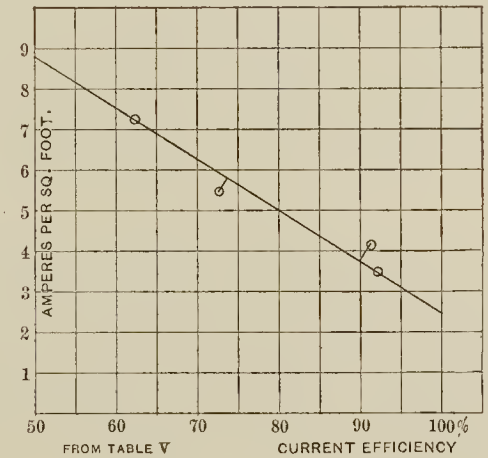

PLATE III.

The relations between the electrode discharge potentials and the efficiencies is shown by a comparison of the data in Table VI:

TABLE VI.

Nature of anode	Ampère hours used	Ampères per square foot		Current efficiency		Discharge potential in volts	
		Anode	Cathode	Anode	Cathode	Anode	Cathode
Cast	1.10	2.75	1.48	88.77%	90.37%	—0.387	+0.252
"	1.76	2.75	1.48	91 00	83.49	—0.337	0.212
"	0.39	2.75	1.48	82.80	94.29	—1.237	0.252
"	2.3	4.12	4.12	89.77	94.62	—0.290	0.273
"	3.29	4.12	4.47	92.61	88.94	—0.463	0.246
"	.4	7.25	4.42	62.93	93.51	—1.580	0.228
"	.3	4.12	2.21	82.96	91.10	—0.360	0.253
Rolled	.43	3.10	3.10	9.01	57.39	—1.880	0.142
"	3.01	3.17	3.17	27.08	33.18	—1.883	0.118

The cathode and anode efficiencies of Table VI are plotted, with their respective electrode potentials, in Curves I and II of Plate IV.

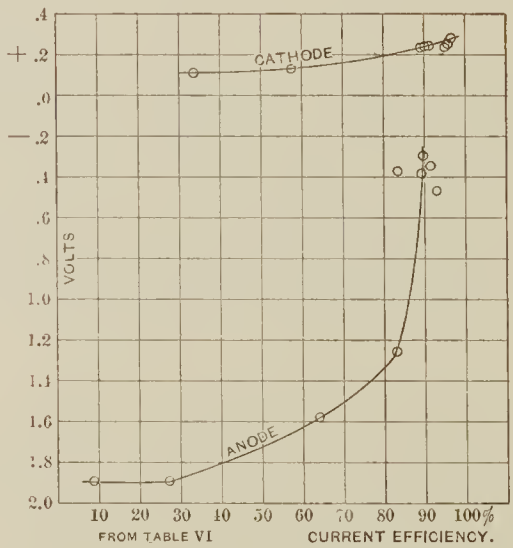

PLATE IV.

It seems that the highest cathode efficiency is obtained when the cathode discharge potential lies between + 0.22 and + 0.29 volt.

The anode voltage increases very fast as the anode efficiency begins to diminish. The results show that an efficiency of corrosion exceeding 90 per cent cannot be expected if the anode voltage is allowed to get much above — 0.46 volt.

Pfanhauser* states that nickel ammonium sulphate between nickel electrodes can be decomposed with a bath tension of about one volt; but that in a short time the current strength falls very fast to almost nothing, while the bath tension rises to two volts. He also states that there are two polarizations, one of about one volt and the other near two volts. He ascribes this high electrode tension and polarization to the formation of a coating of nickelic hydroxide on the anode. He has shown that nickel ammonium sulphate is a complex salt, and that in concentrated solutions $Ni(SO_4)_2$ ions are liberated at the anode. These $Ni(SO_4)_2$ ions may attack the nickel electrode and form two molecules of $NiSO_4$, or they may react with water, forming sulphuric acid, nickelous sulphate and oxygen. The $Ni(SO_4)_2$ ions may also unite with $NiSO_4$, forming $Ni_2(SO_4)_3$. He thinks that the nickelic sulphate is then decomposed by hydrolysis, yielding nickelic hydroxide, sulphuric acid and oxygen. He says that in strong acid solutions, however, the nickelic sulphate decomposes as follows:

$$\begin{matrix} Ni = SO_4 \\ \diagdown \\ \quad SO_4 \\ \diagup \\ Ni = SO_4 \end{matrix} + H_2O = \begin{matrix} NiSO_4 \\ \\ NiSO_4 \end{matrix} + H_2SO_4 + O.$$

He has tested the chain

$$Ni/(NH_4)_2\,Ni(SO_4)_2/Ni(OH)_3,$$

and finds that it gives 1.075 volt. For this reason he believes that the high polarization is due to the nickelic hydroxide on the anode.

In all of Pfanhauser's measurements either electrolytic or rolled nickel anodes were used. His explanation seems to fit the facts very well when these electrodes are used, but they do not explain the data obtained with cast-nickel anodes. In one experiment with a cast anode, after electrolysis at an anode density of 4.12 amp. per square foot for seventeen hours, the discharge potential was only — 0.47 volt, the polarization only .74 volt and the electrode tension 1.19 volts. In this experiment the anode efficiency was 92.6 per cent. This seems to show that with proper conditions, when cast anodes are used, the electrolysis may be

* Pfanhauser, Zeitschrift für Elektrochemie, 7, 698 (1901).

continued for any length of time (especially when the solution is occasionally stirred) with a polarization considerably below one volt and with an electrode tension of about 1.2 volts.

Under certain conditions the cast-nickel anodes seem to become passive (possibly due to the formation of a coating of oxide, as suggested by Pfanhauser), and in all these cases the efficiency of corrosion immediately drops to a low value. This is not always due to the current density or to the composition of the electrolyte. The following is an experiment showing this passive state: A current was passed through the small plating cell for three hours. During this time the anode density was 4.12 amp per square foot. The anode potential at the beginning was — 0.439 volt, and at the end — 0.447 volt. The electrode tension was 1.1 volts throughout the run, and the polarization remained near — 0.721 volt. At the end of three hours the electrodes were removed, washed in distilled water, dried and weighed. An anode efficiency of 91.3 per cent was obtained. After the electrodes were weighed, they were replaced in the same electrolyte, and the current started at the same current density as before. The electrode tension rose to 2.2 volts, the anode potential to — 1.5 volts and the polarization to — 1.84 volts within fifteen minutes. After three hours the electrode tension was 2.3 volts; anode potential, — 1.68, and polarization, — 1.987 volts. The anode efficiency had dropped to 65 per cent.

When the anode potential suddenly rises, it may generally be brought back to its former value by removing it from the electrolyte, cleaning in a mixture of sulphuric and nitric acids, rinsing in distilled water and then replacing it in the cell. After the electrolysis has continued for thirty minutes, with an anode discharge potential of — 0.45 volt or lower, I have never known it to change to a much higher value at the same current density.

The rise in anode potential in these experiments must, then, be due to some treatment it received outside the cell, while washing in distilled water, drying in an air bath, cooling in a dessicator and weighing. One would at once say that the passive state of the electrode was caused by the formation of a film of oxide on its surface during the process of drying and weighing. This is possibly true, but the following experiment is not explained by this assumption.

The average electrode tension was 2.2 volts, the anode potential

remained near — 1.78 volts and the polarization — 2.03 volts. A current density of 2.75 amp per square foot was used. After two hours' electrolysis, the electrodes were removed and weighed. An anode efficiency of 87.88 per cent was obtained. The electrodes were then replaced in the electrolyte, and a current of the same density started through the cell.

The electrode tension was surprisingly only 0.9 volt, the polarization 0.606 volt and the anode potential — 0.331 volt. The temperature of the electrolyte at this time was 28.5° C, but cooling it to 15° only raised the electrode tension 0.1 volt. After continuing the electrolysis sixteen hours, the electrode tension was 1.0 volt, polarization — 0.729 and anode discharge potential only — 0.444 volt. The anode efficiency was about 89 per cent. After the electrodes had been removed, rinsed in distilled water, dried and weighed, they were again placed in the same electrolyte. In a very few minutes the electrode tension was 2.1 volts, the polarization — 1.87 and the anode potential — 1.6 volts. After four hours' run the anode efficiency was 78 per cent.

From the results of these measurements the fact is shown that satisfactory operation of a nickel-plating solution depends to a large extent on the character of the anode employed. This is a fact which has been recognized by platers as a result of practical operation. It might be a natural supposition that the best results should be expected with the purest anode material, but this apparently is not the case. It appears that the presence of copper is advantageous to a certain extent, and it is quite likely that certain other impurities which are usually present in cast nickel may be equally advantageous. It has been shown that rolled nickel or electrolytic nickel are decidedly unsatisfactory for anode service, and the reason that the cast nickel shows a superiority may be due to the impurities or to a different physical structure, which gives rise to a great porosity and roughness of the surface, and thereby a greater actual surface area.

In electroplating operations the cathode has naturally been the point to which most attention has been given in the production of certain qualities of deposit, but a study of the conditions at the anode is equally important, for if the corrosion at that point is satisfactory the cathode will largely take care of itself. The lack of efficient corrosion at the anode results in an excess of acid being

formed, which, diffusing to the cathode, causes a lower efficiency at that point as well. A change of efficiency at the anode is in a very short time made apparent by a similar change at the cathode. In instructions which have been published from time to time for operating nickel-plating tanks, the voltage which is necessary for plating is referred to in an indefinite way. This is probably due to the fact that the electromotive force required under different conditions is of a considerably different value, so that no definite rules can be laid down. The electroplater can obtain an efficiency of 90 per cent or more if cast anodes are used, with an anode density of about 5 amp per square foot. The best method of obtaining a check on his efficiency is by the determination of the anode discharge potential. This should not be allowed to reach a greater value than — 0.45 volt.

It is possible, however, that the study of such single potential is too much of a laboratory test, and requires apparatus which is not at his disposal. A study of the total polarization pressure, however, while not being as definite in the indications as a study of the individual electromotive force at the electrodes, will serve as a means for determining whether the cell is operating properly. When the polarization goes much above 0.75 volt, the assumption is justified that the anode is not corroding properly, and, on the other hand, if the polarization is below 0.70 volt the efficiency at the anode is as high as can be obtained. The means for measuring this polarization is at the disposal of most electroplaters, the method consisting in connecting a voltmeter to the anode and cathode terminals while the current is flowing and then suddenly interrupting the current and noting the pressure between the electrodes immediately after. This reading should be made as quickly as possible, as the polarization decreases rapidly after interrupting the current.

In conclusion, I wish to thank Prof. C. F. Burgess for his valuable suggestions and assistance throughout this work, which was proposed by him.

Laboratory of Applied Electrochemistry,
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DISCUSSION.

MR. MCA. JOHNSON: This article is interesting to me, for it follows along lines which I have worked on in the past, namely, the study of the anode potential and the cathode potential by means of a standard electrode in determining the factors of electrolytic work. I doubt though that the ordinary electroplater is going to install an Ostwald calomel standard electrode and a $150 potentiometer to determine electrode potentials. However, the way pointed out in the last page of Professor Brown's paper is a fairly accurate method and a practical one. This article, in my opinion, could be criticized in the following way: that not enough analyses were made of the electrolyte.

The current efficiency at the cathode is dependent upon the percentage of nickel at the cathode and also the percentage of free hydrogen ions. If the percentage of free hydrogen ions increases to a certain limit, we do not get metallic nickel, but we get pure hydrogen. As the percentage of hydrogen ions decreases we get an increasing percentage of nickel and a decreasing percentage of hydrogen; but, nevertheless, we always get hydrogen at every potential, under every condition, as can be shown by the fact that we have a low current efficiency at the cathode. To investigate on electroplating work I think about 250 analytical determinations would be necessary. I have had a good many more than that made on electro-refining work, where the conditions are entirely different—the nickel contents of electrolyte, instead of being 30 grams to the liter is 150 to 200 grams of metallic nickel per liter; the current density is 10 to 30 ampères per square foot, and the temperature as high as possible within practical limits. Nevertheless this article is of much value, even though it is imperfect in the fact that it gives little analytical data.

PROF. C. J. BURGESS: The addition of analytical data such as Mr. Johnson recommends would undoubtedly make this paper more complete. If such completeness had been aimed at, however, this paper could not have been prepared in the time which has been available, as it would be an investigation of very considerable length.

Mr. Johnson does not think that the "calomel" electrode as a standard for the measurements of simple potentials is a practical

instrument for technical men, but upon this point I am inclined to disagree with him; we have found it of great use in the laboratory on account of its simplicity of construction and operation. A potentiometer arrangement which we have employed in connection with this electrode was made in our laboratory and at a cost less than one-tenth the amount which Mr. Johnson names.

The measurements described in this paper were made on a nickel-plating solution, such as is used every day by the electroplater and no chemical analysis of such solutions were made. The approximate composition was known, however, inasmuch as after each run a solution freshly made up was employed. The only chemical tests which were made during the operation of the cells were such as are commonly made by the electroplater to determine the acidity or the alkalinity of the bath.

PRES. RICHARDS: The statement made on page 93 of Dr. Brown's paper is very interesting: "It appears that the presence of copper is advantageous to a certain extent, and it is likely that certain other impurities which are usually present may be equally advantageous." The idea that the presence of an impurity in the anode may be advantageous is odd at first, but I think may be explained by the fact of local action—the increase of local action upon the anode; that where copper is mixed with the nickel the local action of the solution will probably cause the nickel to dissolve in larger proportion than it would by electrical action alone. We find, for instance, that pure zinc is very slightly attacked by acids, but attacked rapidly if there is a small amount of another metal present to facilitate the solution, so I think the chemical solution of the anode is probably facilitated by the presence of copper or other impurity.

DR. RUDOLPH GAHL: I should not think that the impurities of the nickel could cause much local action. Nickel causes strong local action on account of its low overvoltage on metals of higher overvoltage; for example, on copper. But the metals which are generally contained in nickel as impurities have a higher overvoltage than nickel has, and, therefore, I do not think that they can cause local action.

PRES. RICHARDS: You state that they have a lower overvoltage effect?

DR. GAHL: Yes, sir.

PRES. RICHARDS: Platinum with zinc intensifies the local action, but platinum has a lower overvoltage effect than zinc, so that it is rather the short-circuit effect of which I am thinking that the presence of the impurity in the body of the anode may have.

DR. GAHL: It depends on the amount of the overvoltage. Platinum has a very low overvoltage, and, therefore, causes an especially great local action; the other metals of higher overvoltage than platinum when deposited on zinc do not cause so much local action as platinum does. For example, the local action caused by copper is less than that caused by nickel, and the local action of nickel is much less than that of platinum, therefore, you cannot cause local action on nickel at all by copper, nor by lead nor by zinc, if these metals are deposited upon nickel.

MR. C. J. REED: How is the overvoltage determined? The overvoltage of platinum, for instance, or nickel?

DR. GAHL: Overvoltage of a metal is the excess of voltage which is required for developing hydrogen on this metal over that required for developing hydrogen on platinized platinum.

MR. REED: It is based, then, upon platinized platinum as a standard?

DR. GAHL: Yes; we have no other standard. It is theoretically possible that there is another metal which requires a still lower voltage than platinum does for the electrolytic development of hydrogen. But we do not know such a metal and therefore take that metal which requires the lowest voltage of all known metals.

MR. REED: I have never been able to find two pieces of platinized platinum that acted alike, so I do not see that there is any standard if that is the case. If that is the only standard we have, it seems to me there is none.

DR. GAHL: Yes, there are differences, but they are not so very great, the difference between platinized platinum and common unplatinized platinum is not more than 0.09 volt. On the other hand, the difference between zinc and platinum is 0.7 volt, and, therefore, great, compared with the variations of platinum. So, though platinum is not a perfect standard, it is a useful one for many purposes.

MR. REED: I have found the same differences in platinum

depending upon the conditions under which it is used; for instance, with platinum electrodes in sulphuric acid, the overvoltage (voltage required to produce gas on the platinum) would depend on how you apply the current. If you begin with a very small electromotive force, you can gradually increase it up to two volts or in that neighborhood before you get any appreciable current. Then after the film of gas on the surface of the platinum has once broken, the voltage will drop down at once to one and a half volts, and you can continue to deposit hydrogen at one and a half volts. Now, what is the overvoltage of platinum in that case? A theoretical requirement of the electrochemical electromotive force would be 1.47 volts. Now, you can get gas at one and one-half volts, or you can get it at two volts under those two different conditions. Which is the overvoltage of platinum, .03 volt or .53?

Dr. Gahl: I do not know this experiment which Mr. Reed refers to, but I have made similar experiments with different kinds of lead and almost the same conditions. I have electrolyzed, for example, two cells with sulphuric acid, one with a pure lead, the other one with an antimonious lead cathode, and always obtained higher voltages for the cell with pure lead. The difference between the two voltages is about the same for all densities of current; therefore, I should think the difference in the overvoltage for these two kinds of metal is the difference you find here, and I do not see why in replacing the one metal by platinum there should be much difference in the behavior, but I should like to make that experiment myself.

Mr. Reed: That is a very interesting experiment, and it is one that I think ought to be considered in discussing this question of voltage. The facts are as I have stated, that if you electrolyze platinum electrodes in dilute sulphuric acid, beginning with a very low electromotive force and gradually increasing it, not by large steps, but by continuous increments, as, for instance, by using a dynamo in which you gradually increase the electromotive force up to two volts, you can increase it to nearly two volts without getting any perceptible current, that is, without getting more than what is generally called "residual currents." Then suddenly the current will apparently break through a film of gas and gas will appear in spots or patches on the platinum electrode.

Then the voltage goes down immediately. You can continue then to get an evolution of gas with one and one-half volts.

PRES. RICHARDS: Mr. Reed has brought up the question of overvoltage. In a paper which I have prepared to read to-day, I show some experiments where the voltage was increased on platinum electrodes to 110 volts without any evolution of gas, so that we have in that case an overvoltage of perhaps 108.5 volts.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1903, President Richards in the Chair.

A NEW TYPE OF ELECTROLYTIC CELL.

By P. G. Salom

In a paper read at the inaugural meeting of this society, on "The Electrical Reduction of Lead," I promised on some future occasion to give further details of the process described at that time.

I mentioned in that paper that one of the most serious difficulties we encountered, was the incomplete reduction of the ore, apparently independent of current density or the time during which the ore was under current.

We found that this difficulty was due almost entirely to the thickness of the layer of ore, and that when this was materially diminished the reductions rose to 97 or 98 per cent metallic lead and over.

With the type of cell employed at that time, it was manifestly impracticable to use thinner layers, as we were only charging from 12 to 15 pounds of ore, making a layer about ½ inch thick.

This rate of ore charge involved the use of 10,000 cells for an output of 10 tons per day, and the labor, charging and discharging, 2,000 cells per day. As the thickness of the layer was only ½ inch, if we reduced it to 1-10 inch, or lower, the number of cells required was appalling.

Under the circumstances, therefore, there was nothing to do but to materially increase the current density per square foot of cathode surface, and to enormously increase it per pound of ore. This we found we could do economically with the thin layers, and instead of using 12 ampères per square foot, and 1 ampère per pound, we are now using 30 ampères per square foot and 50 ampères per pound, and believe we will reach a current density of 60 ampères per square foot, without materially diminishing the current efficiency, which under present conditions is about 66 per cent.

Then, with 100 of our new cells, which are exactly 6 feet in

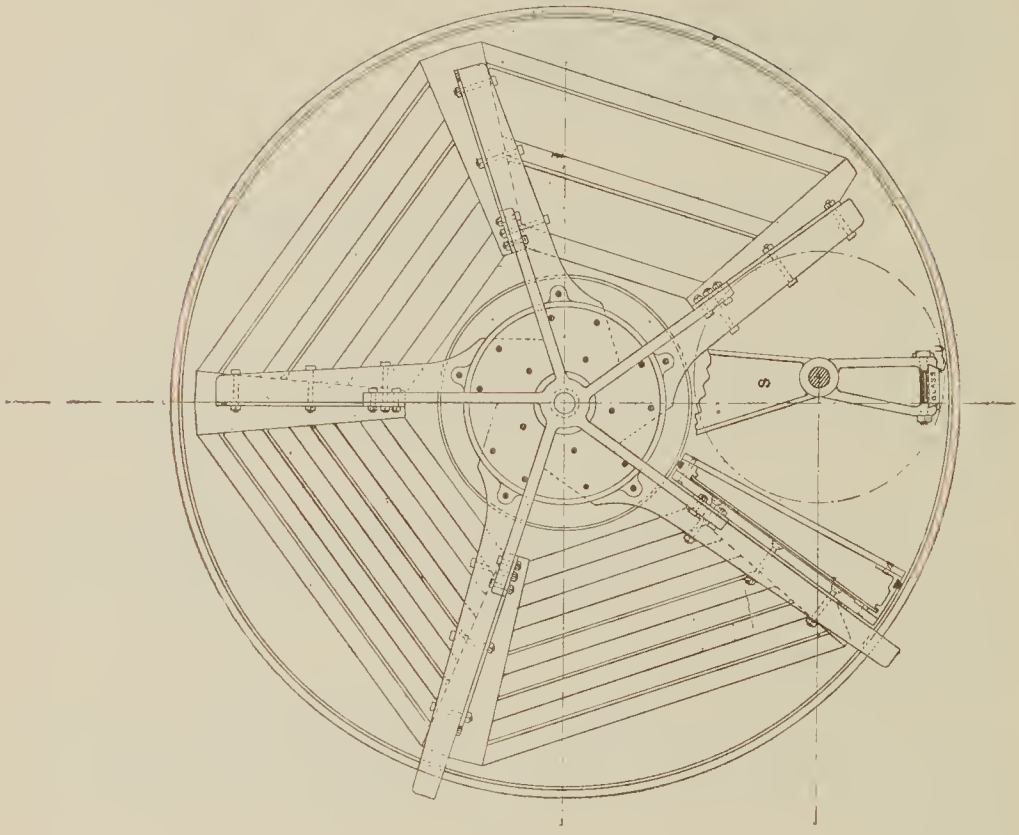

FIG. 1

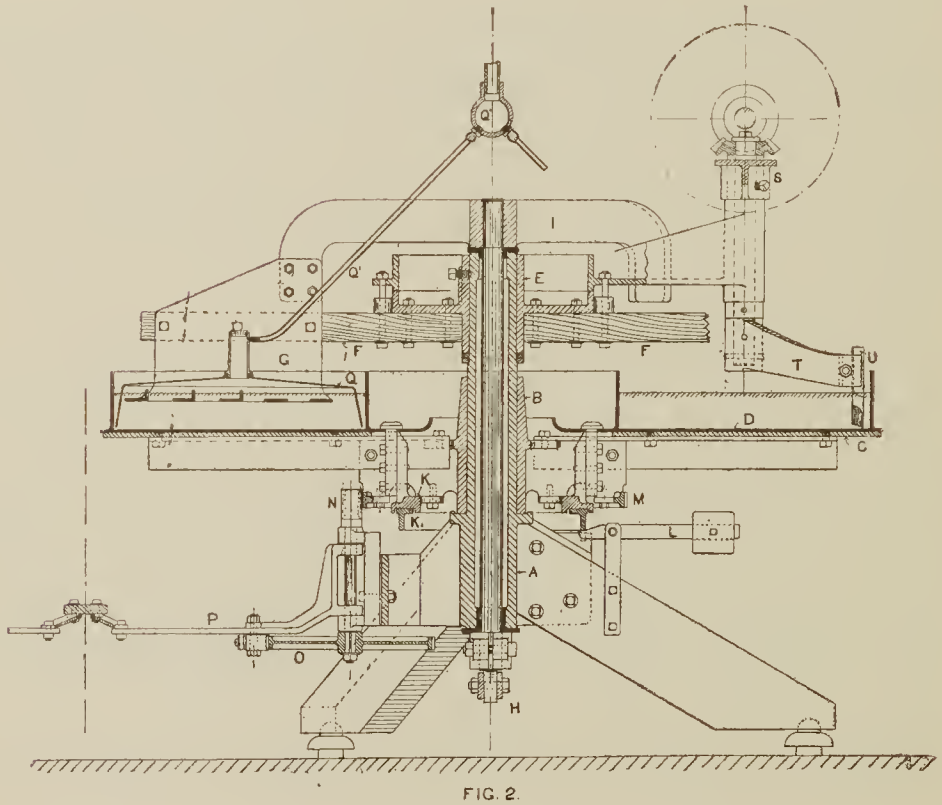

FIG. 2.

diameter, we will be able to produce 10 tons of lead per day, and the five-day rate has been reduced to one and one-half hours, which is the time required per revolution.

One of the greatest advantages of the new cell is that it makes the process continuous. The material to be acted upon may be continuously supplied to the electrode in any given quantity, and at any given rate, and the product formed may likewise be continuously removed without interruption of the process.

The operation of the cell is entirely automatic. The cells are placed in rows of 17 or more each, with a motion rod or bar between them, to which is fastened from each cell a lever actuating a pawl and ratchet with suitable gear wheels, by means of which the cell is rotated at the speed desired.

The ore or substance to be acted upon may be fed into the supply receptacle by a belt or other suitable conveyor, and the only manual labor required is to remove from time to time the resulting product or products of electrolysis accumulating in front of the scraper.

Obviously the apparatus and process are subject to great variation in regard to the nature and composition of the electrodes and the electrolyte, the direction of the current, and the mechanical details of the apparatus.

In the drawing here shown, the supply receptacle and scraper are stationary, and the lower electrode revolves, but it is evident that relative motion between the two is what is required, and that this may be obtained by moving the upper electrode, together with the feed box and scraper, or both electrodes may move in different directions, or at different speeds.

To Mr. Henry G. Morris is due the credit for the mechanical design of the cell.

Referring to the drawings:

Fig. 1 is a plan, and Fig. 2 is a sectional elevation.

A, is a hollow central shaft supported by wooden legs in the form of a tripod, properly insulated from the ground.

On this central shaft a spider B, supports a steel plate C, upon which rests the cathode D, which is in the form of an annular pan.

Above the same central shaft is attached a casting E, carrying wooden arms F, to which the anodes G, are bolted.

The positive terminal H, is an insulated conductor passing through the hollow shaft A, and connected electrically through a second spider I, to the anodes.

The return current passing through the electrolyte and out of the cathode through collector rings K-K′, one of which, K, is attached to the spider B, and the other, K′, supported from the tripod by weighted lever L, and to which ring is attached the negative terminal.

The cathode is revolved by means of a gear M, attached to spider B and pinion N, which in turn is moved by ratchet wheel O and lever P.

Between each segment of the anode rests a hard-rubber gas cover Q, reaching on two sides to the bottom of the cathode, and thus insulating the walls of the same from the anode, and connected by rubber tubes Q′, to a common outlet Q″.

Referring to Fig. 1, one segment is left open for the accommodation of the supply receptacle or feed box R, and scraping device S, which in this case consists of a revolving arm T, carrying cutter U.

DISCUSSION.

Mr. C. J. Reed: Is the operation complete in one revolution of the cathode?

Mr. Salom: Yes, sir.

Mr. Reed: That is, in one hour and a half?

Mr. Salom: One hour and a half. That may be increased or diminished.

Mr. Reed: What does the stirring?

Mr. Salom: There is no stirring.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1903, President Richards in the Chair.

ELECTROLYSIS OF SODIUM HYDROXIDE BY ALTERNATING CURRENT.

By Carl Hambuechen.

The title of this paper may, perhaps, be considered a misnomer, inasmuch as it deals with a method for producing electrolysis by connecting an electrolytic cell directly to a source of alternating pressure rather than with the electrolytic effects of a symmetrical alternating current.

Electrical energy is being generated and distributed in large amounts in the form of alternating current, and the means for transforming it into a unidirectional current becomes a matter of moment to the electrochemist. Such transformation is usually effected by the rotary transformer type of apparatus, and it is proposed to point out here a method whereby such apparatus may be dispensed with. This may be done by the use of aluminium as one of the electrodes in a cell in which electrolytic decomposition is to be effected.

At the first meeting of this Society it was pointed out in a paper, submitted jointly by Professor Burgess and the writer, that aluminium in certain fused salts presents, in a marked degree, the property of readily permitting the passage of current toward it and interposing a high resistance to the flow in the opposite direction. Utilizing this property, an electrolytic rectifier, using aluminium and iron electrodes in a fused sodium nitrate electrolyte, has been developed. It was found also that aluminium could be used in a like manner in various other fused electrolytes, one of which is sodium hydroxide.

While aluminium is actively corroded by sodium hydroxide in the presence of water, the observation was made that it is almost completely stable in contact with a fused sodium hydroxide, and that consequently an aluminium vessel might readily serve for containing this substance. Not only is aluminium unattacked in this condition, but in attempting to use it as the anode it immediately strengthens its protective coating so as to oppose with a considerable resistance the passage of current.

Curve No. 1, plotted with the volts pressure applied to an aluminium anode as ordinates, and with current as abscissæ, shows that the aluminium allows almost no current to flow until the pressure has exceeded a value of 40 volts. After such pressure has been reached, the protective coating becomes broken down and the current flows readily.

By employing two aluminium electrodes in the same electrolyte, and applying an alternating pressure, curve No. 2, of a somewhat similar form, is derived. It will be seen that the breakdown pressure with an alternating current is less than with a direct, due largely to the fact that the pressures given are effective pressures, the maximum pressure being considerably higher than that indicated by the alternating-current voltmeter. Inasmuch as the electrolysis of sodium hydroxide requires a pressure of about four volts, it will be seen that such pressure is well within the range of the aluminium.

An experiment was performed to determine whether a combination of an aluminium and an iron electrode in fused sodium hydroxide could be employed simultaneously as a rectifying cell and as an electrolytic cell for the production of metallic sodium. The results which were obtained seem to indicate that sodium may be produced, and with almost as high an efficiency, when connected to an alternating-current circuit as to a direct-current circuit. The accompanying sketch illustrates the construction of the cell in which this process was carried out:

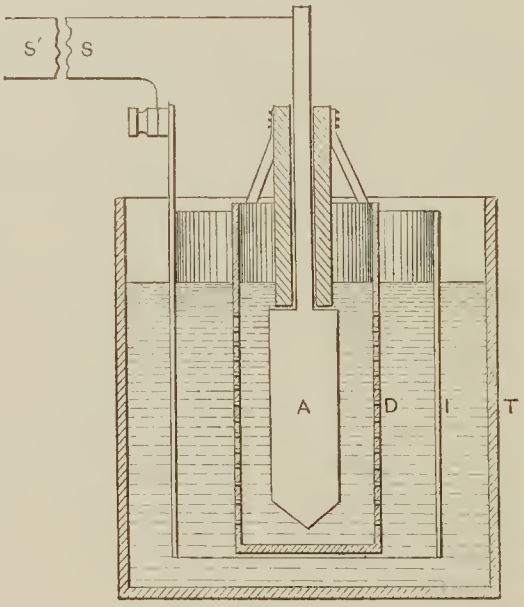

FIG. 1.

T is an aluminium vessel in which the salt is fused; I represents an iron electrode surrounding the aluminium electrode A; S represents the secondary of a step-down transformer, the pressure at its terminals being about six volts; S′ is the primary of the same transformer connected to a 110-volt circuit; D represents a diaphragm surrounding the aluminium electrode and insulated from it by a porcelain sleeve surrounding the upper portion of the aluminium electrode. This aluminium diaphragm was perforated so as to allow a communication of the electrolyte and the passage of the current through it.

A current of 9 ampères, as indicated by a direct-current instrument, was passed into this cell, and after some time globules of fused metallic sodium appeared on the surface. The cell was operated for several days, and a considerable quantity of metallic sodium was collected. It was found that careful regulation of the temperature was necessary to produce a large yield, but, other than this, the cell required no attention. At the end of the run the aluminium electrode showed almost no corrosion, the only indication of it being at the point where the aluminium was in contact with the porcelain.

As a result of a run to determine the amount of corrosion of the aluminium, it was found that an electrode 1.5 inches long and .5 inch in diameter lost about one-half gram during a run of 50 ampère hours. The sodium, upon being liberated, rose to the surface of the liquid, and was prevented from diffusing over to the cathode by means of the aluminium diaphragm. The short-circuiting between the aluminium anode and the diaphragm was prevented by the porcelain insulating sleeve.

To determine the effectiveness of the aluminium in preventing the current flowing from it to the electrolyte, current and pressure curves were obtained by means of a Blondel oscillograph. One of these curves is shown in Fig. 3, curve *(a)* being the current curve and *(b)* the pressure curve at the cell terminals. The portion of the current curve below the axis represents a leakage current, which may be due to the small particles of sodium adhering to the electrode and to a small leakage which naturally takes place from such an electrode. This portion of the curve represents a loss of energy which is wasted, unless its heating action is useful in maintaining the cell at the proper temperature. The portion of

the curve above the axis represents the useful current. From a measurement of the areas of these curves, the current efficiency may be calculated. The efficiency, as computed in this manner, was about 73 per cent. The alternating pressure which was applied had a peaked wave form, and previous measurements showed that a sinusoidal or flatter wave form allowed a higher efficiency to be obtained, so that a value higher than that given can undoubtedly be realized.

What is apparently a new feature in the construction of electrolytic cells is embodied in the apparatus here described in the form of the aluminium diaphragm. The suggestion has been made by Professor Burgess that aluminium may be a suitable diaphragm material when used in electrolytes such that its property of opposing the flow of current from it may be utilized. The perforations in the aluminium diaphragm may be small and at the same time allow a high current density without the current passing through the aluminium conductor. The diaphragm will not,

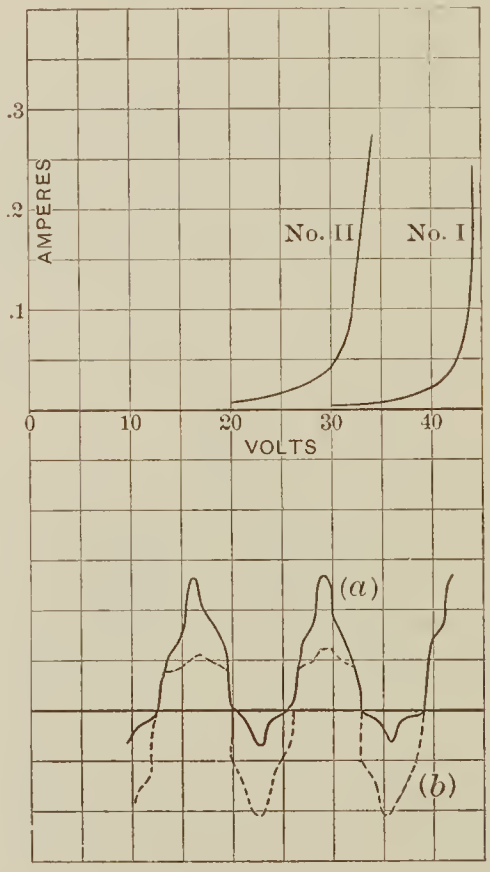

FIG. 2.

under such circumstances, take part in the conduction of the current, and the efficiency may therefore be higher than when iron or other similar metals are used. In the aluminium diaphragm employed in these experiments it was found that no corrosion occurred except at the surface of the electrolyte, where the diaphragm projected from the fused salt. There was a slight corrosion at this point, which could probably be accounted for by the absorption of moisture by the electrolyte when it was allowed to cool.

The same method of operation of an electrolytic cell might be applied in obtaining various electrolytic products other than sodium. While the current efficiency is less than if a direct current be employed, this loss may be partially balanced through avoiding the losses of a rotary converter. The additional loss caused by the leakage current is made manifest by the heating of the electrolyte, which may be an advantage or a disadvantage, depending upon the nature of the electrolyte.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1903; Vice-President Bancroft in the Chair.

THE ELECTROLYSIS OF WATER (Paper II).

By Joseph W. Richards and Walter S. Landis.

At the last meeting of the American Electrochemical Society we called attention to an experiment performed by us in which we showed the application of Ohm's law alone to dilute sulphuric acid for voltages up to 3.5 volts. The work at that time was not complete, and a new series of experiments have been made, the results of which are here presented.

The conditions governing the current used in this work have been fully presented and discussed in the above paper;* they will not be repeated here. We found the cell used in the previous work (the tube 8.75 meters long) unwieldy, and decided to modify it. Instead of making the length of the cell the principal factor in its resistance, as before, we now made the area. By using short capillary tubes, we were enabled to get the required resistances without the inconveniences of the long tube.

The cell used in these experiments consisted of two electrode vessels, connected by a capillary tube, the length of which could be varied to obtain the required resistance. The tube was carefully selected, so as to have a uniform bore. The area of the bore was accurately measured by means of mercury, the tube being filled with mercury and the area calculated from the length of the tube and the weight of the mercury which it contained. From this data, and Kohlrausch's values for conductivity of the various electrolytes used, the resistance of the cell was calculated.

In the course of our experiments we found that there are two very important factors to be taken into account, viz.: the current used and the size of the electrodes. Strictly speaking, these two factors are not entirely independent of each other, but we did not have the means at our command to determine their relation, although we have reason to believe that such a relation exists.

* Tranactions, Vol. III, p. 105, *et seq.*

The size of the current which can be used depends apparently on the amount of decomposition which can be taken care of by the dissolved gases in the solution. On account of the very small amount of diffusion which can possibly take place with the cell which we used, the diffusion current may be left out of consideration. The current was regulated by the resistance interposed by the cell, which could be varied to suit the electrolyte used. The size of the electrodes is also an important factor. There seems to be a certain minimum size which is necessary in order that the products of decomposition may be taken care of (re-combined) as fast as formed. The relation of their size to the current employed, or, stated otherwise, the maximum allowable current density, was not determined.

The detailed experiments are as follows:

Experiment I.—Electrolyte, 0.1 per cent sulphuric acid. Electrodes, platinum, area approximately 25 square centimeters each. Specific resistance of 0.1 per cent sulphuric acid is 197 ohms (Kohlrausch). Resistance of cell calculated from above 275,800 ohms. The current values and the applied voltage, together with the resistance calculated therefrom, are given below in the respective columns headed volts, micro-ampères and resistance:

Volts	Micro-ampères	Resistance
0.50	1.47	274,800
1.00	3.22	310,000
1.48	5.32	278,000
2.00	7.00	285,000
2.50	8.96	279,000
3.00	10.85	276,000
	Average	283,800

The above readings are plotted in Plate I, together with the line representing the current which would flow as calculated from Kohlrausch's value for the conductivity of the electrolyte. The solid curve represents the above current values, and the dotted line those calculated from the theoretical resistance of the cell.

Experiment II.—Electrolyte, 1.00 per cent sulphuric acid. Electrodes, platinum, area approximately 50 square centimeters each. Specific resistance of 1.00 per cent sulphuric acid, 21.93

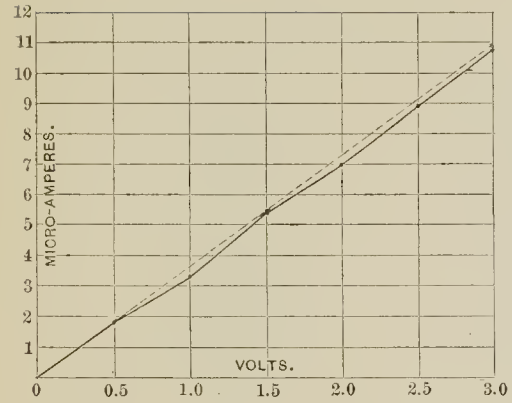

PLATE I.

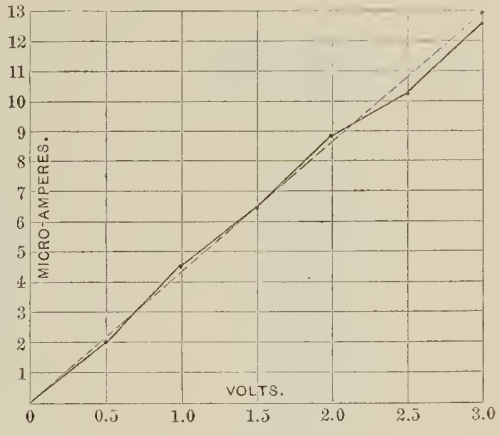

PLATE II.

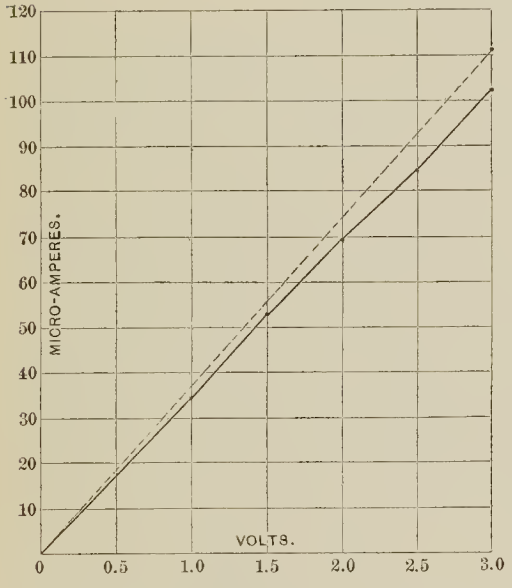

PLATE III.

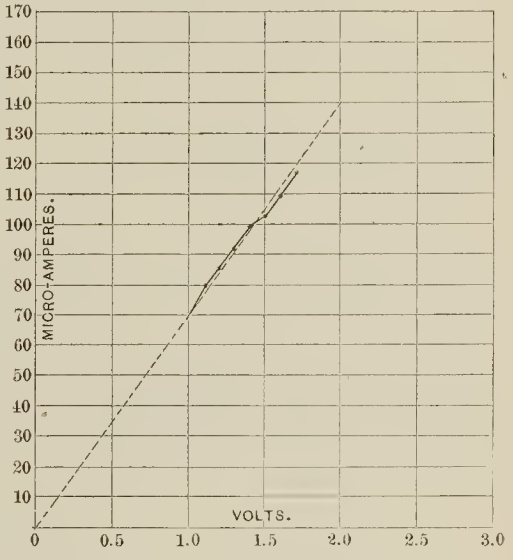

PLATE IV.

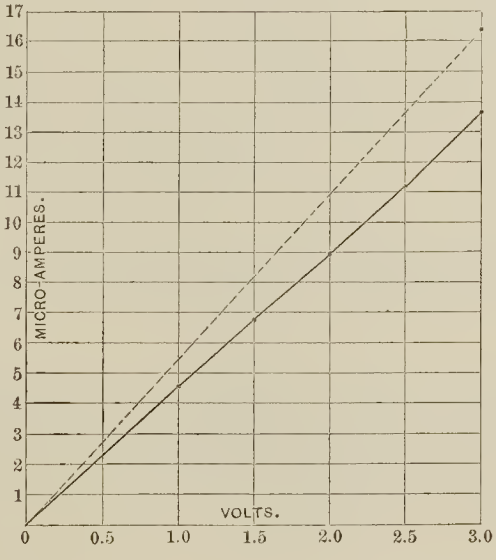

PLATE V.

ohms (Kohlrausch). Resistance of cell calculated from the above, 233,000 ohms.

Volts	Micro-ampères	Resistance
0.50	2.03	246,000
1.60	4.48	223,000
1.50	6.44	232,000
2.00	8.82	229,000
2.50	10.29	242,000
3.00	12.60	238,000
	Average (not including the first reading, because the voltage was somewhat doubtful)	232,800

These results are plotted in Plate II in the same manner as those of Experiment I.

Experiment III.—Electrolyte, 10.00 per cent sulphuric acid. Electrodes, platinum, 157 square centimeters area each. Complete depolarization was effected between each reading by short-circuiting the cell, and the readings are those obtained immediately on closing the circuit. The specific resistance of 10.00 per cent sulphuric acid is, according to Kohlrausch, 2.567 ohms. Resistance of the cell, calculated from this value, is 27,200 ohms.

Volts	Micro-ampères	Resistance
1.0	36.05	28,530
1.5	52.22	28,720
2.0	68.95	29,000
2.5	84.49	29,610
3.0	102.13	29,400
	Average	29,000

Plate III shows a graphical representation of these results, together with the theoretical current plotted from Kohlrausch's value.

Experiment IV.—Electrolyte, 30.0 per cent sulphuric acid. Electrodes, platinum, area 94.5 square centimeters each. Specific resistance of 30 per cent sulphuric acid, according to Kohlrausch, 1.358 ohms. Resistance of cell, calculated from the above data, 14,300 ohms.

Volts	Micro-ampères	Resistance
1.00	69.16	14,460
1.11	79.38	14,100
1.20	86.24	13,930
1.30	92.75	14,040
1.40	99.12	14,150
1.50	102.48	14,620
1.60	109.55	14,610
1.70	117.60	14,450
	Average	14,295

The above results are plotted in Plate IV. This electrolyte was examined more closely than the others, because it is acid of maximum conductivity, and therefore presents almost exactly the crucial conditions for this method of investigation. We would call attention to the close coincidences between the theoretical and calculated resistances.

Experiment V.—To further test the theory advanced in our paper of last April, concerning this current, which is proportional to Ohm's law, and in which we stated that this proportionality could only exist when the products of decomposition were completely re-combined by the process of depolarization, without being set free, we determined to try a different electrolyte, sodium carbonate. The products of electrolysis are the same as with sulphuric acid, and therefore, if our theory is correct, it should apply to this solution also. The electrolyte consisted of a solution containing 0.053 per cent ($\frac{N}{100}$) sodium carbonate, the specific resistance of which, according to Kohlrausch, is 1,047.7 ohms, from which the calculated resistance of the cell is 18,320 ohms. Electrodes, platinum, 157 square centimeters area each.

Volts	Micro-ampères	Resistance
1.0	4.55	22,000
1.5	6.72	22,300
2.0	8.96	22,300
2.5	11.13	22,400
3.0	13.51	22,200
	Average	22,300

The results are plotted in Plate V. As the solution was very carefully made up, and as the difference between the observed and calculated values is far too large to be ascribed to inaccuracy of the instruments, we have reason to believe that the specific resistance, as given by Kohlrausch, is possibly at fault. The specific resistance calculated from the average of the above readings would be 1,275 ohms.

The above method of investigation has appeared to us to be of probable use in determining specific resistances of electrolytes from which oxygen and hydrogen are evolved under ordinary conditions. It is convenient, inasmuch as it allows the employment of direct current, requires no resistance in the circuit other than that of the cell or adjustment of the same and the required calculations are easily performed. Below will be found a comparison of our determinations of the specific resistances of the sulphuric acid solutions we used, with the values given by Kohlrausch for the same solutions. Our values are calculated upon the average of the resistances as given under each experiment:

	Specific Resistance	
Concentration	Calculated from experiments	Kohlrausch
0.1	202.7	196.9
1.0	22.05	21.93
10.0	2.74	2.56
30.0	1.354	1.358

In conclusion, we will sum up the conditions which should be observed in using this method:

I. The current must be kept within the limit of that which can be completely depolarized by the gases in solution in the electrolyte.

II. The electrode surface must be large enough to allow this depolarization to take place simultaneously with the decomposition.

III. The current readings are the maximum values obtained immediately on closing the circuit, the electrodes being free from polarization before connection is made.

SUMMATION OF DIRECT AND POLARIZATION CURRENTS.

The results so far recorded are the currents obtained at the moment of completing the circuit; in general, it took five to seven

seconds for the needle to come nearly enough to rest to get a fixed value. For high resistances and with large electrodes this current decreases only slowly, and more slowly the larger the electrodes. With currents of 15 micro-ampères or more, using electrodes of 25 square centimeters each, the current falls off as time elapses. For instance, using 1.50 volts on a 1 per cent H^2SO^4 solution, the readings were:

At	15″	30″	45″	60″	75″	90″	300″
Micro-ampères	33.9	31.8	30.7	30.2	29.9	29.6	28.4

When the current thus falls off, there is back electromotive force found on cutting off the voltage and short-circuiting the cell. Putting in a reversing switch, so as to be able to pass the polarization current through our ammeter and so to measure its amount, we determined the maximum polarization current which could flow at the end of the corresponding times given above. Each polarization current was determined by a separate test, the cell being short-circuited long enough to completely depolarize between tests. The maximum value of the polarization current was:

Voltage applied	15″	30″	45″	60″	75″	90″	300″
Micro-ampères	7.4	9.4	10.6	11.2	11.5	11.9	12.5

If these values are added to the directly-measured currents, their sum is found to be 41.3, 41.2, 41.3, 41.4, 41.5, 40.9 micro-ampères, thus showing a practically constant sum.

The interpretation of these results is as follows: The current passing on first closing the circuit is 41.3 micro-ampères (average of the constant sum). This would make the resistance $1.50 \div 0.0000413 = 36{,}320$ ohms. The resistance calculated from the steady current obtained with larger electrodes was 36,280 ohms. Therefore, at the first moment, all the applied voltage is used up in overcoming ohmic resistance, and $C = V \div R$. As the current falls, however, the voltage absorbed in overcoming ohmic resistance is less, because the current is less, and V^c is always equal to CR. But the applied voltage is constant, therefore a constantly-increasing voltage is being absorbed, in doing chemical work. At 300 seconds, for instance, $V^c = 0.0000284 \times 36{,}320 = 1.02$, and therefore $1.50 - 1.02 = 0.48$ volts is being absorbed,

or disappears in chemical work. The amount of energy being converted into Joulean heat in overcoming ohmic resistance is $V^c \times C = C^2R = 0.0000284 \times 1.02 = 0.0000290$ watts [$(0.0000284)^2 \times 36{,}320 = 0.0000290$ watts]. The amount of energy of the current not being used in overcoming ohmic resistance is the rest of the energy of the current, viz.: $0.0000284 \times 0.48 = 0.0000136$ watts, and this amount of energy can only be consumed in doing chemical decomposition. But, since every coulomb actually decomposing water must supply 1.5 joules of energy to do it (Thompson's rule), every ampère actually producing ultimate decomposition must supply 1.5 joules per second, or 1.5 watts will be thus consumed. Therefore, the number of ampères producing decomposition is $\frac{0.0000136}{1.5} = 0.0000091$. Therefore, out of the total current passing through the electrolyte, 28.4 micro-ampères, 9.1 micro-ampères produce decomposition, while 19.3 do not. Or, looking at it in another way, the whole current passes, the whole current evolves Joulean heat $= C^2R$ in overcoming the ohmic resistance, the whole current produces O and H at the electrodes, but $\frac{19.3}{28.4}$ of the gas thus evolved recombines at the electrodes with gases in the solution, and gives back the energy absorbed in producing it (perfect depolarization), while $\frac{9.1}{28.4}$ of the gas remains uncombined, and goes into solution (ultimate decomposition).

The above explanation, based only on the energy necessary to do a fixed amount of work, is practically a means of resolving voltages. *Part* of the current may be regarded as passing without any voltage of decomposition (V^d) being absorbed for it, the other part in its passage absorbs $V^d = 1.50$ volts. $(\frac{19.3}{28.4} \times 0) + (\frac{9.1}{28.4} \times 1.5) = 0.48$ volts absorbed in decomposition, reckoned on *all* the current passing. Therefore, the total voltage, $1.50 = V^c + V^d = CR + V^d = 1.02 + 0.48$.

The voltages thus absorbed in decomposition at the different times of the test were calculated out, and then measured by balancing them against another electromotive force. The value of the polarization voltage was found to correspond with the V^d calculated, showing that polarization was produced agreeing with V^d, the voltage actually absorbed in producing decomposition. It follows, that if a part of the products of electrolysis are recombined, thus virtually absorbing no V^d from the current, and

another part, say, $\frac{1}{x}$ are not, then the observed voltage actually consumed in decomposition will be $\frac{1}{x}$ of the theoretical voltage of decomposition of the compound. Such an explanation completely accounts for the value of V^d in the electrolysis of water using voltages up to 1.5 volts.

RESIDUAL CURRENTS.

It is not the intention to report here *in extenso* on this subject, but to report one experiment which gave very interesting results. Two electrodes with some 70 square centimeters surface were placed 1 centimeter apart, in 30 per cent sulphuric acid. The resistance of the cell was therefore extremely small, say, 0.02 ohm. The surface of the acid was covered with oil, to prevent absorption of gases or water from the air. A very small voltage was first applied, and then gradually increased, keeping the current at about 100 micro-ampères constantly. The voltage was thus increased until at 1.8 volts the current passing remained constant (five hours), at 91 micro-ampères, without evolution of gas or apparent change of any kind. Our view is that this constant residual current was practically all producing decomposition, the gases produced being absorbed by the electrolyte.

When the applied voltage was lowered to 1.00, the constant residual current was 5.6 micro-ampères; an approximate calculation from Bigelow's results on constant residual current at this voltage* gave 4.6 micro-ampères as the current we might have been expected to get. It thus appears, that the constant residual currents are greater for greater applied voltages.

If the electrodes carrying such a residual current are removed from the cell, heated red hot and then replaced, the current flowing does not go back to the original value which it had on first starting the experiment, but remains practically what it was when the electrodes were removed. This seems to point to a change in the electrolyte itself, or in its capacity to depolarize, as the cause of the running down of the current, and not to a change in the electrodes themselves. In other words, so-called increasing polarization in this case is not a progressive change of the electrodes themselves, but is due to a decreasing ability of the solution in

*Journal of Physical Chemistry, December, 1902.

contact with the electrodes to recombine with the ions and so perform the function of depolarization. Bigelow, in his work on residual currents, removed the "polarized" electrodes, wiped them dry, and then replaced them, and observed very little change; he ascribed this to the idea that he was not able to wipe off the gases condensed in the pores of the electrodes, and which he supposed accounted for their apparent polarization. The truth is, that the decreased current is not due to a change in the electrodes, but to a change in the solution; which latter change is, to all appearances, the exhaustion of its gases (oxygen and hydrogen) held in solution.

MINIMUM VOLTAGE FOR VISIBLE EVOLUTION OF GAS.

The visible evolution of gas is not a function of the applied voltage alone. In most of our experiments, voltages from 1 to 4 were applied to the cell without any trace of evolution of gas, and by using a very high electrolyte resistance, as much as 110 volts direct current was applied to a 10 per cent solution of sulphuric acid without causing visible decomposition. From a great number of experiments, the conclusion is evident that current density at the electrodes is the prime factor in determining visible evolution of gas.

With one electrode one centimeter square, and the other a point ⅛ millimeter in diameter by 1 millimeter long, gas can be obtained on the point at an applied voltage of 1.12 to 1.15, no matter whether the point is anode or cathode, and no matter whether it is platinum or gold. Increasing the size of the point required a corresponding increase in the value of the applied voltage necessary to produce gas. With electrodes of equal size no gas can be obtained below 1.5 volts applied.

Measurements of current and area show that approximately 5 micro-ampères per square millimeter (5 ampères per square meter) are necessary for the visible evolution of gas. If the current density is greater than this on one electrode and less on the other, gas will appear only on the first. The only rational explanation of this we can offer is that the rate of diffusion and solution of gases in the electrolyte is approximately measured by the ability of each square millimeter of electrode to transmit the

gaseous products of 5 micro-ampères into solution. If the current exceeds this, the gases cannot dissolve as fast as they are being generated, and therefore the difference must be eliminated as free gas. Since the heat of solution of hydrogen and oxygen is very small, it makes little difference to the energy absorbed from the current whether they are evolved free or go into solution; the principal difference from the energy standpoint is when the gases are recombined, and converted back again into water, by the complementary gas being already in the solution.

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DISCUSSION.

MR. C. J. REED: I regret that I did not have time to read this paper before the meeting, and was out while it was being read, so I would like to ask what size the electrodes were which were used in this experiment?

DR. J. W. RICHARDS: In those given in the paper the electrodes were 15 square centimeters each. The external resistances were very small and the voltage given is that applied to the cell measured across the terminals of the cell.

MR. REED: It seems to me that these results are exactly what we should expect would necessarily occur with platinum electrodes of that size. The very minute currents which are produced through this resistance with 3 volts, or even 100 volts, would be such as would correspond to what we call residual currents, and the additional electromotive force above that required for decomposing water would produce only an insignificant current—only 0.0001 ampère through such a resistance. No visible gas could be expected on platinum electrodes having a surface of 15 square centimeters with a current of 0.0001 ampère. The probability is that, with such a small current, it would require months or years to saturate the electrode with the gases, even if no gas escaped. Was any visible gas produced in these experiments?

DR. RICHARDS: No visible gas in any of these experiments.

MR. REED: I think not; so it seems to me we could not expect any other result from the action of the platinum plates. The production of gas on a small electrode in connection with a large one with one volt or a little less seems to me also what we should expect, and I think we ought to call that "undervoltage" to correspond with the overvoltage which has been spoken of where the electromotive force required is greater than one and one-half volts. It seems to me that this is explained very easily from the fact that whichever of these gases is evolved in contact with the large electrode, combines with the electrode and forms a compound of platinum with that gas. There is a chemical effect there which evolves heat, or, what is equivalent to that in this case, reduces the required electromotive force. It almost amounts to the same thing as electrolyzing sulphuric acid with two lead electrodes in which you get hydrogen with less than one-half volt very easily.

MR. CARL HERING: The resistance calculated from the data given in the curves, may agree well with that calculated from the specific resistance of the liquid, but it seems that this is to a great extent accidental. I understand that each of the readings plotted in the curves, was taken seven seconds after the circuit had been closed, and that the current diminished rapidly with the time. Now, if the readings had been taken after a different number of seconds, say, after fifteen seconds, or after one second if the instrument permitted it, the calculated resistance would have been very different. There seems to be no real reason why the results should be more correct at seven seconds than at any other period of time; it seems to have been merely because it took about seven seconds before the instrument could be read, and is, therefore, a matter of chance.

I would like to ask how the instruments were connected. In a test of this kind the current flowing through the voltmeter is much greater than that flowing through the apparatus, and the ammeter must therefore be connected inside of that part of the circuit to which the voltmeter is connected, otherwise the ammeter reading will include the relatively large current flowing through the voltmeter. In that case the voltage readings would have to be corrected for the drop of volts through the ammeter. Were these corrections included in the results?

DR. GAHL: Dr. Richards stated that he has measured overvoltages of 110 volts. I should like to ask him about his method of determining overvoltages. I should think that it is an impossibility to determine overvoltages with such an apparatus having a very high resistance. I think that all the voltage is used up by the resistance, so that you do not measure real overvoltages in that way. If you wish to determine overvoltages you must first see that you have gas development; in the second place you must make the resistance as low as possible, or if you cannot do that you have to compare two vessels obtained with cells of the same size, of just the same construction, one of which has a cathode which you wish to compare with the standard electrode, and the other one the standard electrode itself. Of course both electrodes must have the same form and size. You cannot then find such high voltages, you will find only some tenth of a volt or so. I should like to ask Mr. Reed when a low voltage of one-half volt, which he claims is enough to develop gases at the cathode is obtained, which is anode in this case?

MR. REED: Lead.

DR. GAHL: Pure lead?

MR. REED: Both electrodes are pure lead.

DR. GAHL: Anode pure lead, too?

MR. REED: Yes.

DR. GAHL: I cannot understand how gas can develop in this case, perhaps it may come from the sulphuric acid, dissolved gas, set free.

MR. REED: I mean that hydrogen gas is evolved at the cathode, and it continues in unlimited quantities at one-half volt.

DR. GAHL: I never found that.

MR. REED: I would refer you to a paper which I published in the *Journal of Physical Chemistry* about two years ago on that subject, entitled "The Gas Polarization of Accumulators." If there were time I would explain it. We are rather short of time this morning, and as it has already been published, I hardly think I ought to take the time for that.

DR. RICHARDS: In reply to Mr. Reed, in all my experiments with platinum electrodes, with high resistance and small currents, I have not found any chemical effect due to the use of the platinum. I have replaced the platinum by gold; I have taken the

platinum electrode out when it was giving a certain current, and heated it red hot and placed it back again in the solution without any change. I could not find that any change in the amount of current flowing was dependent on the conditions or the kind of the electrode which I was using—whether platinum or gold, or what condition it was in. My explanation of the current passing is, that it is due to the solution of the oxygen and hydrogen formed in the electrolyte and complete depolarization, so that the current passing at the first instant that the circuit is closed. is comparable to the current passing between two copper electrodes in a solution of copper sulphate with complete depolarization and no voltage absorbed in decomposition. As the current passes, and the gas around the electrodes becomes used up, then there is not enough gas to cause complete depolarization and the current naturally falls off, giving you the voltage absorbed in decomposition. The reading was taken at seven seconds, because that was the shortest time in which the ampèremeter came to rest. When the circuit was closed it took seven seconds for the needle to become steady, and that was taken as the maximum current. By plotting the course of fall of current it was seen that that reading was probably 2 or 3 per cent lower than the maximum which might have been obtained at zero time if the current was extended to zero time. So that the observed values are all possibly slightly below the actual value of the current if it could be obtained at zero time on the instant of closing the circuit. By taking the observations, however, at other times—fifteen, thirty and forty-five seconds—and adding to it the polarization current, constants were obtained a little higher than the reading at seven seconds, and which were practically constant throughout the run of five minutes, so that those summated values could be substituted for the theoretical value at zero minutes.

As for the overvoltage referred to in Dr. Gahl's remarks, he says that it should be determined in vessels of the same construction and shape in order to get comparative results. Vessels could be constructed of the same size and shape where these results would none of them give gas at low voltages. He says the resistance must be made as low as possible. Well, here you run against the physical impossibility of making the resistance extremely small. I have not solved that question by myself, but I think there is some mathematical limit at which you can arrive

in reducing the resistance between two electrodes if they are of the same size. I have not quite solved the question, but it seems to me that if two electrodes are of the same size there seems to be some limit as to the minimum resistance which you can get between them. If you make one very small and the other very large, you get entirely different effects, but if you try to get the current density on the two the same, there seems to be a minimum resistance. If you take wires and oppose them to each other and get them very close together the current will not pass between the two ends of the wires, but will jump off from the wire away back from the end. I have observed that over and over again. The minimum resistance seems to be away from the point where the two electrodes are brought closest together. If you increase the surface, so as to reduce the resistance, the current density will fall so low that gas is not evolved until much higher voltages are applied.

DR. GAHL, (Communicated after adjournment): In explanation of my questions directed to Mr. Reed about the conditions under which he succeeded in developing hydrogen at a P. D. of only half a volt, I would state, that by the expression "electrolysis between lead electrodes in sulphuric acid" is generally understood, at least in Germany, the simple cell consisting of two solid lead plates immersed in sulphuric acid. One of the characteristics of this cell is that upon passage of a current the anode very quickly becomes coated with a film of lead peroxide. For example, the term "electrolysis between lead electrodes" as used in the papers of Dolezalek and Nernst on the over-voltage signifies this simple arrangement and takes for granted the film of peroxide on the positive plate. The use of this term seems to me to have caused the misunderstanding of the quoted papers by some American investigators.

Of course a blank lead plate, especially if it has a large surface, has a depolarizing action for some seconds and a spongy lead plate for hours, when used as anode, and it is quite obvious, that in a cell with such an anode (which Mr. Reed used, according to a personal communication) hydrogen may be developed at a very low voltage. If Mr. Reed had used a platinum cathode with such a spongy lead anode he might have developed hydrogen at less than zero voltage, or, in other words, the cell would generate a feeble current.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 19, 1903, President Richards in the Chair.

ON THE SUPPOSED ELECTROLYSIS OF WATER VAPOR.

By F. Austin Lidbury.

The chemical phenomena which accompany the discharge of electricity through gases, in comparison with those connected with the passage of electricity through solutions, have received scanty attention from investigators. It is well known that many compound gases suffer decomposition to a greater or less extent by the discharge of electricity through them, and no less well known that an actual separation of the constituent gases, bearing at least a superficial resemblance to the process of electrolysis in liquids, occurs in certain cases. In the majority of these cases the evidence of separation is purely spectroscopic, the characteristic spectrum of one component gas being observed at the negative electrode, that of the other at the positive electrode. J. J. Thomson,[1] E. C. C. Baly and several other investigators have described striking instances of such phenomena.

The investigation of such separations from the electrochemical standpoint has, however, been meager in extent, and practically confined to the single case of water vapor.

In 1861 Perrot[2] showed that when electric sparks are passed through steam, decomposition takes place along the whole length of the spark; that it varies in amount with the length of the spark, and may exceed by 20 times the decomposition in a voltameter placed in series with the sparking vessel; further, that if the gases from the anode and cathode be separately collected and exploded, so as to get rid of the hydrogen and oxygen present in equivalent proportions—*i. e.,* the decomposed as distinguished from the separated gases—then an excess of hydrogen is left in the tube connected with the negative electrode, and an excess of oxygen in the tube connected with the positive electrode, in amounts practically equivalent to that of the copper deposited in the voltameter.

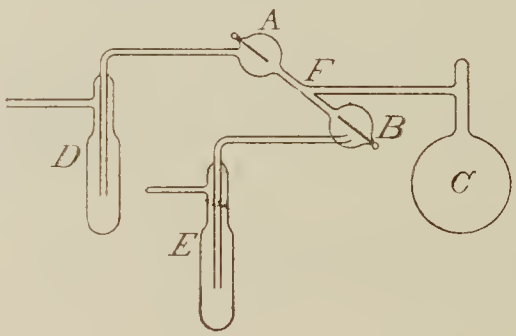
[1] "The Discharge of Electricity Through Gases," pp. 133-136.

[2] Ann. Ch. Ph. (361) p. 161.

This experiment naturally suggested that a process of electrolysis, entirely analogous to that which takes place in solutions, attends the passage of electricity through compound gases, and that an extension of Faraday's law to the latter case was to be expected. And, indeed, the view seems to be widely held at the present day that "in the electrolysis of gases at ordinary or moderate pressures the ions seem to be of the same size and to carry the same charges as in the electrolysis of liquids."[3]

The remarkable and unexpected results obtained by J. J. Thomson in a repetition of Perrot's experiments do not seem to have seriously disturbed this opinion. According to Thomson, the nature and extent of the separation are largely dependent on the length of the spark. Working with steam at atmospheric pressure, he found that with short sparks, having the nature of an arc discharge, the excess of hydrogen appeared at the *anode,* that of oxygen at the *cathode,* thus reversing the effect of aqueous electrolysis. With sparks up to 4 mm length, the amounts of gas separated coincided roughly with those liberated in a voltameter in series, increasing as the length of spark was increased up to a certain limit, then decreasing until at 9 mm spark length it seemed a matter of chance whether hydrogen or oxygen appeared at the anode in excess. At still greater spark lengths the gases appeared at their normal electrodes, and with sparks of from 10-14 mm length the hydrogen and oxygen appeared practically in amounts equivalent to those in the voltameter at cathode and anode, respectively.

More recent experiments on similar lines, initiated by Mr. D. L. Chapman, of the Owens College, Manchester, England, and carried out by him in conjunction with the present author, seem to throw some fresh light on the mechanism of the supposed electrolysis of water vapor. The main features of our apparatus can be easily understood from the sketch.



[3] Louis A. Parsons, Trans. Am. E-C. Soc. III, p. 267.

A stream of water vapor is maintained through the discharge tube A-B by keeping the reservoir C at about 25° C and the condensers D, E in a freezing mixture. The stream enters the tube at F, and the symmetrical construction of the apparatus causes approximately equal quantities of the vapor to flow in the directions F-A, F-B, sweeping out the gases from the two sections of the tube into the condensers. Two continuous-working Sprengel pumps, constructed without rubber, in order to avoid the contamination of the mercury with sulphur and organic matter, and the possible interference of these with the accurate determination of the residual oxygen, permit of the perfect removal of air from the apparatus before an experiment, and of the separate collection and analysis of the gases swept from anode and cathode respectively into the condensers during the passage of the current.

The experiments were carried out as follows: After all air has been carefully removed from the apparatus, the reservoir B is surrounded by a water bath and the condensers D and E by a freezing mixture. The pumps are set in operation, and sparks from an induction coil, provided with a large condenser, are passed through the tube A-B, which is fitted with electrodes of thick platinum wire 25-30 mm in length. A voltameter (nickel electrodes in caustic soda solution) and an air gap, to insure the passage of electricity in one direction only, are placed in the same circuit. Water vapor enters the discharge tube in a rapid stream. The products of decomposition in the two halves, FA, FB, of the tube are swept forward into the separate condensers and pumped out into specially-constructed collecting tubes, in which the hydrogen and oxygen present in equivalent proportions are combined from time to time by sparking, and in which the residual excess of hydrogen or oxygen can be determined at the end of the experiment, both directly and (as a check) by explosion.[4]

Preliminary experiments having shown that residues comparable in amount to the gases liberated in the voltameter were left, quantitative experiments were begun. The first experiments showed a quantity of hydrogen separated at the cathode, varying between one-fourth and one-half of the quantity collected at the cathode of the voltameter. The current of water vapor in these experiments was slow, ice alone being used to cool the condensers.

[4] For a more detailed description of the apparatus, mode of working, precautions necessary, etc., see Trans. Chem. Soc., vol. 81, p. 1306.

On substituting a freezing mixture of finely-powdered ice and salt, so as to accelerate the speed of the stream of vapor, we found that the ratio of hydrogen separated in the spark to hydrogen from the voltameter rose to a number varying from 1 to 2. Probably a rapid stream of vapor tends to prevent the spontaneous mixing (by convection and diffusion) of the separated gases in the tube. In a series of experiments, with a spark length of about 100 mm, the width of the spark tube being 8 mm, and the inlet tube being placed as nearly as possible midway between the two electrodes, the following numbers were obtained:[5]

No.	Hydrogen from voltameter c. c.	Hydrogen from cathode of discharge tube c. c.	Ratio
1.	1.088	1.163	1.07
2.	1.108	1.08	0.975
3.	1.338	1.155	0.863
4.	0.889	2.14	2.41
5.	0.696	0.827	1.188
6.	1.76	3.63	2.06
7.	1.57	1.76	1.121

Still more striking are the results obtained when the inlet tube enters the spark tube, not in the center, but in close proximity to the cathode.

(Inlet tube about 10 mm from cathode bulb.)

No.	Hydrogen from voltameter c. c.	Hydrogen from cathode of discharge tube c. c.	Ratio
1.	1.23	4.19	3.41
2.	0.992	5.95	6.00
3.	0.376	2.75	7.31

On placing the inlet tube as near as possible to the anode bulb, or (which comes to the same thing) reversing the direction of the current in the tube used for the last-mentioned set of experiments, we found a great diminution in the amounts of residual gas from

[5] In all cases the amount of oxygen obtained from the anode was also measured, and in many cases both H and O were measured directly and by explosion; the agreement in all cases was very satisfactory, though the oxygen figure usually was slightly less than half the hydrogen; this we attribute to the formation of ozone and the consequent oxidation of the mercury in the pumps. The discrepancy was not entirely removed by sending the gases over heated silver gauze on their way to the pumps.

cathode and anode, and on examination the gas from the anode turned out to be *hydrogen,* that from the cathode *oxygen.* This result recalls forcibly the curious reversal noticed by Thomson in passing from long sparks to short sparks.

Three experiments gave hydrogen at the anode and oxygen at the cathode, as shown by qualitative tests. In one case we made an analysis of the gases, with the following result:

H from voltameter	1.54 cc
H from anode (directly measured)	0.86 cc
(by explosion)	0.78 cc
2 × O from cathode (directly measured)	0.38 cc
(by explosion)	0.33 cc

Here, owing to the long time which was required to collect such small residues of the gases, the absorption of oxygen by the mercury of the pumps becomes many times greater than in the other experiments (see note 5).

Throughout these experiments every effort was made to secure uniformity of conditions (velocity of water vapor, uniformity of discharge, etc.), and to vary only the position of the inlet tube. Under these circumstances, we believe that we may legitimately conclude that *in the partial decomposition of water vapor by the electric discharge the hydrogen and oxygen liberated tend to separate and to take up different positions in the tube, the hydrogen collecting at both anode and cathode and the oxygen in the middle of the tube.*

From the above-described experiments, it is obvious that any slender grounds which Perrot's experiments may have appeared to afford for the belief that an electrolytic decomposition of water vapor, entirely analogous to the electrolysis of water, takes place are entirely the result of the particular conditions under which he worked. The mere separation of far larger quantities of hydrogen and oxygen in a discharge tube than are simultaneously obtained from a voltameter in the same circuit does not, however, exclude the possibility of making some such assumption in a modified form. Thomson has advanced excellent evidence[6] in support of the view "that an electrified particle of gas is the center

[6] "Discharge of Electricity Through Gases," pp. 11-17.

of an aggregate of some kind, which is very large compared with the dimensions of a molecule," and there seems no reason for insisting that a gaseous ion must carry the same charge as a corresponding ion in solution. The fact, however, that in the decomposition of water vapor by the electric spark hydrogen tends to collect not only at the cathode, but also, though to a less degree, at the anode, entirely wipes out the supposed similarity between the two classes of phenomena, and leaves the mechanism of the separation of hydrogen and oxygen in the vapor an open question. At present there would seem to be far too little data for the construction of a satisfactory theory to explain the result above mentioned, but it should be noted that Thomson has brought forward some evidence which points to the possibility that a hydrogen ion may carry either a positive or negative charge. He observed that a capillary tube containing hydrogen, on the passage of the spark, gave spectra at the anode and cathode, in which the relative brightness of the lines differed. Some assumption of this kind might possibly explain the unexpected behavior of hydrogen described above. Facts, however, rather than hypotheses, are what are needed in this particular branch of electrochemistry.

DISCUSSION.

Mr. F. A. J. Fitz Gerald: In the only determinations of oxygen given, I notice that twice the oxygen is 0.36 cc for the mean of the two determinations, while the hydrogen from the anode is about 0.82, *i. e.*, the oxygen is 50 per cent less than it ought to be according to theory. Could Mr. Lidbury give us the quantities determined in any other experiment?

Mr. F. A. Lidbury: I may say in answer to Mr. Fitz Gerald that this diminution in the amount of oxygen is a phenomenon that we noticed throughout the whole of the experiments, and the reason why it amounts to such considerable proportions in this particular experiment is that the amount of residual oxygen is so extremely small that a very small amount of absorption of oxygen by the mercury of the pumps or by any organic matter that happens to be present makes a considerable difference in the final result. However, in the other experiments in which we were

dealing with considerably larger residues of oxygen the absorption does not assume relatively such formidable proportions. For instance, to take the second column of results, in which the ratios are larger than in any other set of experiments, we get the following:

No.	Hydrogen	Oxygen + 2
1	4.1 cc	4.22 cc
2	5.9	5.74
3	2.75	2.60

In experiments where we obtain larger quantities of residual gas than in the one to which Mr. Fitz Gerald referred, the error is practically negligible in comparison with the amounts of the residual gases themselves.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 19, 1903, President Richards in the Chair.

NOTE ON METALLIC DIAPHRAGMS.

By Eugene A. Byrnes.

In a paper read by me at the Niagara meeting one year ago, a diaphragm which resists the action of fused sodium hydroxid was referred to, but not described in detail. A complete description of this diaphragm will be found in United States patent 735,464. The diaphragm consists of magnetite crushed to sand and interposed between concentric cups of perforated sheet iron. While a lump of magnetite conducts like a metal, a diaphragm of finely-divided magnetite has a very high ohmic resistance and does not perceptibly act as a bipolar electrode, even with large potential gradients. A diaphragm of this character was used in molten sodium hydroxid in July, 1896, the crushed magnetite being mixed with a small amount of Portland cement and water before filling it into the space between the perforated iron cups. The use of magnetite followed and was suggested by the action of a wall of finely-divided iron, the particles of which were found to become quickly coated with ferro-ferric oxid when in molten sodium hydroxid. During the years 1896 to 1900 the magnetite diaphragm was employed in a series of experiments on voltaic cells with fused electrolytes, and especially in thesis work in the Graduate School of Columbian University. A similar diaphragm, consisting of crushed magnetite supported between thin vertical sheets of wood, was employed in the electrolysis of an aqueous sodium chlorid solution. A loose diaphragm layer of the crushed magnetite was also floated on a mercury cathode. It was found that the magnetite could be replaced by other materials. Vertical walls of finely-divided lead and coke were used in aqueous solutions of various electrolytes, the physical condition of the material substantially preventing the diaphragm from acting as a bipolar electrode.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 19, 1903, President Richards in the Chair.

THE THERMOCHEMISTRY OF THE THEORY OF ELECTROLYTIC DISSOCIATION.

By Joseph W. Richards.

HEAT OF IONIZATION.

The theory of electrolytic dissociation assumes that in dilute solutions of electrolytes the salts are already potentially split up into their positive and negative ions. The first time that I read this statement of the theory, my first thought was: "Where does the energy come from to cause this dissociation?" This query has been firmly lodged in my mind ever since, and has not been satisfactorily answered by the numerous treatises on electrochemical theory which have since appeared.

The heat of solution in excess of water is usually not a large quantity. The molecular heat of formation of solid potassium chloride is, for instance, 105,700 calories, while if this is dissolved in excess of water 4,500 calories are absorbed. If, then, we assume that the solid salt is composed of undissociated molecules, and the dilute solution of ionized molecules only, then the heat absorbed in the process of ionizing the solid molecules cannot be over 4,500 calories, and therefore bears no quantitative relation at all to the heat of formation of the solid molecules. In fact, we have been overlooking the physical change of state, for the solid salt certainly absorbs heat in changing to the liquid or gaseous molecule in which it occurs in solution, and this change is responsible for part of the 4,500 calories absorbed in the act of solution. The heat of ionization of undissociated molecules of KCl in solution into completely ionized molecules can therefore be but a part of 4,500 calories, if it has any real value at all, and the ultimate conclusion is evident that, whatever the energy required to ionize molecules of salt in solution may be, it is not of the same order of magnitude, nor can it be in any way identi-

fied with the heat of formation of the salt from its constituent elements. It follows that the act of ionization, whatever it may be, is certainly not a destruction or dissociation of the compound *qua* compound, but that from the energy standpoint potassium chloride is as really a compound of potassium and chlorine when ionized in dilute solution as when in the solid condition.

There has been a great deal of uncertainty about this question, and the leading exponents of the dissociation theory leave the subject in a very hazy condition. To remedy this, we must stop thinking that a molecule ceases to be a compound when it is dissolved in dilute solution, or ionized. Whatever the ions are, they are not the chemical constituents from which the compound was formed, and the separation of the molecule into ions is not a destruction of the compound or a resolution of it into its chemical constituents. Ostwald says in his "Grundlinien der Anorganischen Chemie," 1900, p. 210: "Auch in *festen* salzen, die nicht elektrolytisch dissociirt sind, befinden sich die Bestandtheile dem Ionenzustande viel näher, als dem der freien Elemente. Dies geht daraus hervor, dass der Übergang der festen Salze in den Ionenzustand bei der Auflösung in Wasser im allgemeinen nur unbedeutende Wärmewirkungen (meist sogar Wärmeaufnahmen) ergiebt." In other words, Ostwald recognizes that since solid salts, which are not electrolytically dissociated, dissolve in water with very slight thermal effects, that the solid molecule of an undissociated compound, is nearer to the ionized condition than to the constituent elements from which it was formed. If we turn this statement around, it is that the condition of complete ionization is much nearer to the undissociated solid molecule than it is to the free constituent elements of that molecule.

What then is the ionized condition? We can say with certainty, for one thing, that it is a condition of the compound, and not a condition in which the compound has ceased to exist and is resolved into its constituent elements. What is then the heat of ionization? It is the heat absorbed in a change of state of the compound, and is, as far as we can gather, more a physical change of state than a chemical one. It must not be confounded with the heat of solution; for that includes the change of state from the solid molecule to the dissolved ions; neither can it be com-

pletely identified with the heat of dilution, for while during dilution molecules in solution become ionized, yet there are possibly other operations included, such as the making or decomposing of hydrates in solution, and the heat of solution is thus seen to be also a complex quantity.

Arrhenius has calculated heats of ionization thoretically from thermodynamic considerations, from the change in value of the dissociation constant with temperature. He makes them to be negative quantities even in case where the heat of dilution is positive. It therefore would follow, if these calculations are to be relied upon, that the heat of dilution consists of an absorption of heat due to ionization plus an evolution of heat due to combination with water. In any case, we are no nearer the solution of the riddle than before.

There is one thermochemical law which gives us pretty firm ground to build upon, viz., the observation that the heats of formation of salts in dilute solution are plainly additive in their nature. This means that the heat of formation of potassium chloride, for instance, is composed of the sum of one value characteristic of potassium and one characteristic of chlorine. All potassium salts therefore differ from all sodium salts, in their heat of formation to dilute solution, by a constant difference, the difference between the constants of potassium and of sodium; while all chlorine salts differ from all bromine salts by a constant difference—the difference between the constants of chlorine and of bromine. This law is in general true, and places the thermochemical constants of the heat of formation of salts to dilute solutions in exactly the same category as the equivalent electrical conductivities of dilute solutions, their specific gravity, specific optical refractive power and some other physical properties. The truly additive nature of the heats of formation of salts in dilute solutions is a law of the deepest meaning for thermochemistry.

If we consider a dilute solution as containing only ionized molecules, then the heat of formation may be considered, in light of the above thermochemical law, as simply the sum of the heats evolved in the passage of each constituent of the salt from its ordinary molecular condition into the state of being a dissolved ion. The thermochemical constant of a metal would then be regarded as the heat evolved in its passage from the ordinary

molecular free state into the state of combination as a dissolved ion. This quantity has been called by Ostwald *the ionization heat* of the elements, which, it will be observed, is using the term with an entirely different meaning than was given it, as we have been so far considering it. The ionization heat *of a compound* is the heat necessary to resolve its dissolved un-ionized molecule into its ions—which operation is not a resolution of the compound into its constituents, and has therefore nothing to do with the heat of formation of the compound. The ionization heat *of an element* is the heat given out in changing it from a *free,* molecular element into the state of a *combined* dissolved ion. The act of combination is involved in the latter act of ionization, and the term ionization here no longer refers to the electrolytic dissociation of the compound.

Considering the term "ionization heat of the elements," in the sense above given to it, and further considering it as equivalent in value to the thermochemical constants of the elements, we are led to some interesting conclusions. It would follow from this that elements exist in two conditions, viz., the uncombined state and the combined state. Passage into the combined state is accomplished by a change in the intrinsic energy which is characteristic once for all of the element, for a given valency, and independent of any reciprocal action towards the other element or elements with which it is combined; and this combined state is only perfectly attained in dilute solution. Ions in solution are in this view atoms of the element which have passed completely into the "combined" condition, and in doing so have given out their contribution towards the heat of formation of the compound.

The heats of formation of salts to dilute solutions always give us the sum of the separate heats of combination of its separate ions and their "heats of ionization." (K, Cl, aq) = 101,200 calories expresses the fact that the sum of the heats evolved by 39 grammes of solid potassium becoming ionized and 35.5 grams of chlorine gas becoming ionized, is that many calories. (K^2, S, O^3, aq) = 274,600 calories expresses the sum of the heats of ionization of 2K-solid and of SO_3 gas (assuming those to be the ions), plus the heat of formation of SO^3 gas. The only difference between the thermochemical constants and the heats

of ionization would be in the case of complex ions, such as SO^3 for instance, in which case the thermochemical constant for SO^3 would be its heat of ionization *(i. e.,* passage from the state of SO^3 gas to SO^3 ion in dilute solution) plus the heat of formation of SO^3 gas from its elements.

In a few cases, such as iodine and mercury, we know approximately the amount of heat necessary to convert the ordinary free element into atoms. I^2 gas = 2I gas absorbs 28,500 calories, but takes place only at a red heat. Hg (liquid) = Hg (monatomic gas) absorbs 13,560 calories, taking place at 355°. We may therefore go slightly further than Arrhenius in these cases, and say that if Hg (liquid) = Hg ion + 20,500 calories, that therefore Hg (monatomic gas) = Hg ion plus 20,500 + 15,560 = + 34,060. This calculation is not exact, because the latent heat of vaporization of mercury at 18° is not exactly the same as at 355°, being probably somewhat greater. This quantity would be the real heat of ionization of the element, that is, the heat evolved in conversion of one free gaseous atom into one combined dissolved ion. If this could be determined for a number of elements, it is very likely that some generalizations might become evident. This is the only basis on which the true ionization heats of elements can be determined, and to deduce them from present data we must know more of the latent heats of fusion and of volatilization of the elements.

Assuming that the heat of formation of salts to dilute solutions represents the heat of formation of the ions from the elements, and further assuming as the basis of calculation the value of the mercury sulphate electrode—0.89 volt, giving the thermochemical constant of mercury—20,500 calories, we can construct the following table of thermochemical constants, which shows the contribution which each base or acid radical (forming from its elements) furnishes towards the heat of formation of the compound, dissolved to dilute solution.

THERMOCHEMICAL CONSTANTS OF BASES.

		Per Formula Given	Per Chemical Equivalent
Li (solid)	$= Li^{\cdot}$	+ 62,000 calories	+ 62,000 calories
K (")	$= K^{\cdot}$	+ 61,000 "	+ 61,000 "
Na (")	$= Na^{\cdot}$	+ 56,300 "	+ 56,300 "
Rb (")	$= Rb^{\cdot}$	+ 61,100 "	+ 61,100 "
$N + H^4$ (gases)	$= (NH^4)^{\cdot}$	+ 32,500 "	+ 32,500 "
Sr (solid)	$= Sr^{\cdot\cdot}$	+ 115,600 "	+ 57,800 "
Ca (")	$= Ca^{\cdot\cdot}$	+ 107,000 "	+ 53,500 "
Mg (")	$= Mg^{\cdot\cdot}$	+ 106,800 "	+ 53,400 "
Ae (")	$= Ae^{\cdot\cdot\cdot}$	+ 117,600 "	+ 39,200 "
Mn (")	$= Mn^{\cdot\cdot}$	+ 48,000 "	+ 24,000 "
Zn (")	$= Zn^{\cdot\cdot}$	+ 32,600 "	+ 16,300 "
Fe (")	$= Fe^{\cdot\cdot}$	+ 20,000 "	+ 10,000 "
$Fe^{\cdot\cdot}$ (solution)	$= Fe^{\cdot\cdot\cdot}$	— 12,100 "	— 12,100 "
Cd (solid)	$= Cd^{\cdot\cdot}$	+ 16,200 "	+ 8,100 "
Co (")	$= Co^{\cdot\cdot}$	+ 14,600 "	+ 7,300 "
Ni (")	$= Ni^{\cdot\cdot}$	+ 13,600 "	+ 6,800 "
Tl (")	$= Tl^{\cdot\cdot}$	+ 2,000 "	+ 1,000 "
Sn (")	$= Sn^{\cdot\cdot}$	+ 2,000 "	+ 1,000 "
Pb (")	$= Pb^{\cdot\cdot}$	— 1,000 "	— 500 "
H^2 (gas)	$= 2H^{\cdot}$	— 1,800 "	— 900 "
Cu (solid)	$= Cu^{\cdot\cdot}$	— 17,600 "	— 8,800 "
Pt (")	$= Pt^{\cdot\cdot\cdot\cdot}$	— 81,400 "	— 20,350 "
Hg (liquid)	$= Hg^{\cdot\cdot}$	— 41,000 "	— 20,500 "
Ag (solid)	$= Ag^{\cdot}$	— 26,200 "	— 26,200 "
Au (")	$= Au^{\cdot\cdot\cdot}$	— 93,600 "	— 31,200 "

THERMOCHEMICAL CONSTANTS OF ACID ELEMENTS.

		Per Reaction Given	Per Chemical Equivalent
O_2 (gas)	$= 2O''$	+ 86,400 calories	+ 21,600 calories
Cl_2 (")	$= 2Cl'$	+ 80,600 "	+ 40,300 "
Br_2 (")	$= 2Br'$	+ 66,400 "	+ 33,200 "
I_2 (")	$= 2I'$	+ 28,200 "	+ 14,100 "
F_2 (")	$= 2F'$	+ 107,600 "	+ 53,800 "
S (solid)	$= S''$	— 8,400 "	— 4,200 "
Se (met)	$= Se''$	— 34,000 "	— 17,000 "

THERMOCHEMICAL CONSTANTS OF ACID RADICALS.

		Per reaction given	Per chemical equivalent	Salt formed
O_2 (gas) + H_2 (gas) =	$2(OH)'$	+ 112,200 calories	+ 56,100 calories	Hydrate
S_2 (solid) + H_2 (gas) =	$2(SH)'$	+ 8,600 "	+ 4,300 "	Sulph-hydrate
Se_2 (met) + H_2 (gas) =	$2(SeH)'$	+ 40,000 "	+ 20,000 "	Selen-hydrate
Cl_2 (gas) + O_2 (gas) =	$2(ClO)'$	+ 56,800 "	+ 28,400 "	Hypochlorite
Cl_2 (gas) + $3O_2$ (gas) =	$2(ClO_3)'$	+ 45,600 "	+ 22,800 "	Chlorate
Cl_2 (gas) + $4O_2$ (gas) =	$2(ClO_4)'$	+ 80,600 "	+ 40,300 "	Per-chlorate
Br_2 (gas) + O_2 (gas) =	$2(BrO)'$	+ 59,000 "	+ 29,500 "	Hypo-bromite
Br_2 (gas) + $3O_2$ (gas) =	$2(BrO_3)'$	+ 26,800 "	+ 13,400 "	Bromate
I_2 (gas) + $3O_2$ (gas) =	$2(IO_3)'$	+ 131,800 "	+ 65,900 "	Iodate
I_2 (gas) + $4O_2$ (gas) =	$2(IO_4)'$	+ 107,000 "	+ 53,500 "	Per-iodate
4S (solid) + $3O_2$ (gas) =	$2(S_2O_3)''$	+ 290,600 "	+ 72,650 "	Hypo-sulphite
2S (solid) + $3O_2$ (gas) =	$2(SO_3)''$	+ 304,000 "	+ 76,000 "	Sulphite
2S (solid) + $3O_2$ (gas) + H_2 (gas) =	$2(HSO_3)'$	+ 300,600 "	+ 150,300 "	Bi-sulphite
4S (solid) + $5O_2$ (gas) =	$2(S_2O_5)''$	+ 464,400 "	+ 116,100 "	Pyrosulphite
S (solid) + $2O_2$ (gas) =	$(SO_4)''$	+ 215,800 "	+ 107,900 "	Sulphate
H_2 (gas) + 2S (solid) + $4O_2$ (gas) =	$2(HSO_4)'$	+ 424,000 "	+ 212,000 "	Bi-sulphate
2S (solid) + $4O_2$ (gas) =	$(S_2O_8)''$	+ 318,000 "	+ 159,000 "	Per-sulphate
3S (solid) + $3O_2$ (gas) =	$(S_2O_6)''$	+ 278,500 "	+ 139,250 "	Di-thionate
3S (solid) + $3O_2$ (gas) =	$(S_3O_6)''$	+ 274,800 "	+ 137,400 "	Tri-thionate
4S (solid) + $3O_2$ (gas) =	$(S_4O_6)''$	+ 263,000 "	+ 131,500 "	Tetra-thionate
5S (solid) + $3O_2$ (gas) =	$(S_5O_6)''$	+ 268,000 "	+ 134,000 "	Penta-thionate
2Se (solid) + $3O_2$ (gas) =	$2(SeO_3)''$	+ 243,800 "	+ 60,950 "	Selenite
Se (solid) + $2O_2$ (gas) =	$(SeO_4)''$	+ 147,400 "	+ 73,700 "	Selenate
N_2 (gas) + O_2 (gas) =	$2(NO)'$	— 5,800 "	— 2,900 "	Hypo-nitrite
N_2 (gas) + $2O_2$ (gas) =	$2(NO_2)'$	+ 55,800 "	+ 27,900 "	Nitrite
N_2 (gas) + $3O_2$ (gas) =	$2(NO_3)'$	+ 99,400 "	+ 49,700 "	Nitrate
P (solid) + $2O_2$ (gas) =	$(PO_4)'''$	+ 300,600 "	+ 100,200 "	Phosphate
H_2 (gas) + 2P (solid) + $4O_2$ (gas) =	$2(HPO_4)''$	+ 614,600 "	+ 153,650 "	Mono-H-Phosphate
H_2 (gas) + P (solid) + $2O_2$ (gas) =	$(H_2PO_4)'$	+ 308,600 "	+ 308,600 "	Di-H-Phosphate
As (solid) + O_2 (gas) =	$(AsO_2)''$	+ 206,100 "	+ 103,050 "	Arsenite
As (solid) + $2O_2$ (gas) =	$(AsO_4)'''$	+ 213,300 "	+ 71,100 "	Arsenate
H_2 (gas) + 2As (solid) + $4O_2$ (gas) =	$2(HAsO_4)''$	+ 435,800 "	+ 72,600 "	Mono-H-Arsenate
H_2 (gas) + As (solid) + $2O_2$ (gas) =	$(H_2AsO_4)'$	+ 218,100 "	+ 218,100 "	Di-H-Arsenate
2C (amorph) + N_2 (gas) =	$2(CN)'$	— 68,000 "	— 34,000 "	Cyanide
O_2 (gas) + 2C (amorph) + N_2 (gas) =	$2(CNO)'$	+ 76,000 "	+ 38,000 "	Cyanate
2S (solid) + 2C (amorph) + N_2 (gas) =	$2(CNS)'$	— 34,400 "	— 17,200 "	Sulpho-cyanate
Fe (solid) + 6C (amorph) + $3N_2$ (gas) =	$(FeC_6N_6)''''$	— 98,800 "	— 24,700 "	Ferro-cyanide
Fe (solid) + 6C (amorph) + $3N_2$ (gas) =	$(FeC_6N_6)'''$	— 155,800 "	— 51,900 "	Ferri-cyanide
2C (amorph) + $3O_2$ (gas) =	$2(CO_3)''$	+ 333,400 "	+ 83,350 "	Carbonate
H_2 (gas) + 2C (amorph) + $3O_2$ (gas) =	$2(HCO_3)'$	+ 340,000 "	+ 170,000 "	Bi-carbonate
H_2 (gas) + 2C (amorph) + $2O_2$ (gas) =	$2(CHO_2)'$	+ 211,000 "	+ 105,500 "	Formate
$3H_2$ (gas) + 4C (amorph) + $2O_2$ (gas) =	$2(C_2H_3O_2)'$	+ 242,800 "	+ 121,400 "	Acetate
2C (amorph) + $2O_2$ (gas) =	$(C_2O_4)''$	+ 201,400 "	+ 100,700 "	Oxalate

In using these data, the heat of formation of a compound in dilute solution, from its elements, is the sum of the thermochemical constants of its ions, each in dilute solution; the thermochemical constant per chemical equivalent of each ion, however, being multiplied first by the valence of the ion. If the ions, on electrolysis, appear at the electrodes as the elementary constituents of the compound, then the voltage necessary for decomposition is simply the sum of the thermochemical constants of the ions per chemical equivalent divided by 23,040. If the result of the passage of the current furnishes other products than those at the electrodes, then the heat of formation of these products must be allowed for, and subtracted from the heat of formation of the compound from its elements, in order to find the net work which the current then performs.

It must not be overlooked, either, that the basis or base line on which the table is constructed is an arbitrary one, corresponding to $Hg = Hg'' = -41{,}000$ calories, and that if this value should be really smaller (numerically greater), the thermochemical constants of all bases would be correspondingly decreased, while those of all acid ions would be correspondingly increased, and *vice versa*.

HEAT OF NEUTRALIZATION.

To make immediate and specific application of the principles enunciated in the preceding part of this paper, let us consider the phenomenon of the heat of neutralization of bases by acids, in dilute solution. Passing at once to a concrete illustration, we will take up Thomson's determination of the neutralization of dilute caustic soda by dilute hydrochloric acid. The equation is $2NaOH.400\ H_2O + 2HCl.400\ H_2O = 2NaCl.802\ H_2O +$ 27,480 calories. The heat of neutralization per chemical equivalent of the ions concerned is + 13,740 calories, at 18° C.

In the dilute solution of NaOH we have in the terms of the dissociation theory, ionized molecules of NaOH, viz., Na′ and (OH)′ ions; or we may make the statement broader, and simply say that we have molecules of NaOH in the condition called "ionized," by the dissociation theorists. From the standpoint of energetics, as explained in the preceding part of this paper, we have in that dilute solution simply *combined* Na and *combined*

OH, each of these having contributed its thermochemical constant to the heat of formation of the compound. Similarly, in the dilute HCl, we have H′ and Cl′ ions, or, from the other standpoint, *combined* H and *combined* Cl, forming or constituting the compound HCl.

If these two constituents could be mixed without neutralization taking place, it will be generally admitted that the solution would contain ions of Na•, (OH)′, H• and Cl′, or in other words, *combined* Na, *combined* (OH), *combined* H and *combined* Cl. From the standpoint of the dissociation theory, such a solution may equally well be regarded as composed of dissociated NaCl and HOH molecules, as of dissociated NaOH and HCl molecules; similarly, from the standpoint of energetics, it matters not which view we take of such a mixed solution, from this standpoint, it contains simply Na, OH, H and Cl all in the *combined* state.

If we now assume the neutralization to take place, in this mixed solution, what happens? The dissociation theory explains the action very simply by saying that since the resultant solution contains practically only Na and Cl ions, that the H and OH ions have united to form H^2O, and that the heat of neutralization is the heat of formation of H_2O from H• and (OH)′ ions, and is therefore a constant for any acid neutralizing any base. To this statement, taken literally, I have very little objection, except to the term "heat of formation of water," as applied to the union of H and (OH)′ to form H^2O.

The term "heat of formation of water" is a thermochemical term, implying that the constituents which form the water give up their thermochemical heats of combination and pass from the free state into the state of combination. But no such action, nor even a remotely analogous reaction, takes place when H ions unite with OH ions "to form water." The latter case is not one of thermochemical combination, for the H ions are already in the thermochemically combined state, as HCl, before the act of neutralization, and the OH ions are similarly already combined as NaOH. It is then a fundamental mistake to regard the neutralization as proceeding from an act of combination having the least analogy to a chemical act of combination, or of the neutralization heat having the slightest analogy to thermochemical heat of combination. For, if the H and OH ions have once given

out their thermochemical constants, while entering into the state of combination as HCl and NaOH, they cannot give them out again, or any part of them, in any further act of combination. The formation of liquid H^2O from H and OH ions is therefore not a chemical act of combination, and the neutralization heat is not in any sense thermochemical heat of combination. The heat of neutralization, therefore, not resulting from chemical combination, must be *physical* in its nature.

The standpoint of energetics leads to the same view. Whatever the condition of molecules of HCl and NaOH in dilute solution may be, they are still *compounds,* and their constituents are all in the *combined* condition. After neutralization, the Na and Cl are still in the combined condition, as NaCl, and the H and OH are still in the combined condition, as HOH. There has been therefore no change in the condition of any of the constituents named analogous to a change from the free to the combined condition, because they were all in the chemically combined condition before the act of neutralization and all in the combined state afterwards. The heat evolved in neutralization would be, therefore, as far as chemical combination occurs, zero, and its source must be a physical one.

The analogy between the molecular condition of a substance in the state of dilute solution, and the molecular condition characteristic of the gaseous state, furnishes the solution of the problem. We do not know exactly what the molecular structure of solids and liquids is, but it is essentially different from that of gases in the property of filling only a fixed maximum space, while gaseous molecules tend to occupy an indefinitely large space. Solid NaOH has a fixed minimum of specific gravity, at its melting point, where the molecules are as far apart as they can get from each other and the mass still retain the condition of solid material; liquid NaOH has a fixed minimum of specific gravity, at its boiling point, where the molecules are as far apart as they can get from each other and the mass still retain the condition of liquid material. If we force the material to occupy a larger space, its molecules pass into the condition characteristic of a gas.

Solution is a process by which the spatial relations of the molecules of the dissolved substance may be indefinitely extended, and by which, therefore, the substance takes on the molecular

condition of the gaseous state. A cubic centimeter of solid NaCl dissolved in a cubic meter of water passes as certainly into the gaseous condition as if it had been vaporized, for the molecules of salt are further apart in this dilute solution than they would be in vapor of NaCl. I need scarcely take the time to prove this proposition arithmetically, since this view of the subject is qualitatively and quantitatively proven by the phenomena of osmotic pressure. The facts of osmotic pressure prove that a substance in dilute solution exerts pressure which has all the characteristics of gas pressure, and agrees quantitatively with the pressure which the material could exert in the state of gas if occupying the volume of the solution, but in the gaseous state. The temperature co-efficient of the osmotic pressure, moreover, agrees with the gas co-efficient. I believe that all will agree, at least, on the very close resemblance or analogy between the gaseous state and the state of being in dilute solution, and a consideration of the heat of neutralization from the point of view taken in this paper tends to confirm their practical equivalence.

Since the molecule of NaOH in dilute solution exerts osmotic pressure, analogous to its being in the gaseous condition, and the same is true of the molecule of HCl, the two solutions, if mixed without neutralization taking place, would exert in the mixed condition osmotic pressure as in each solution separately, all the constituents being in the "ionized" condition and exerting osmotic pressure analogous to gaseous pressure. When neutralization takes place, only Na and Cl are left in dilute solution, and exert the osmotic pressure, the pressure due to the H and OH has disappeared, co-incident with these passing into the condition of liquid water. The act of neutralization is therefore merely the passage of H and OH from the combined state in dilute solution, in which condition they exert gaseous, osmotic pressure, into the combined state as liquid water, in which they exert practically no osmotic pressure. The change is exactly analogous to the change from the gaseous into the liquid condition, and is therefore the equivalent of the condensation of water vapor into the liquid state. The source of the heat of neutralization is therefore the physical change of state of HOH from the gaseous to the liquid condition, without any heat of chemical combination being concerned or even possible, because the ingredients, H and OH,

are as much in the *combined* condition before the act of neutralization as after it.

To verify this statement quantitatively, we need to take into consideration the fact that 2 NaOH.400 H^2O will occupy 7.2 liters (if the molecular weights be expressed in grammes), and the NaOH will exert an osmotic pressure of 12.34 atmospheres. The 2 HCl.400 H^2O occupies an equal volume, and the HCl exerts a similar osmotic pressure. After the mixing of the solutions the osmotic pressure exerted by each molecule in solution is halved, but the total osmotic pressure is 12.34 atmospheres. After neutralization, there remains only the osmotic pressure of the 2NaCl in the 802 H_2O, which is 6.15 atmospheres, the osmotic pressure of the H and OH, together equal to 6.19 atmospheres, disappearing because of the condensation of the water to the liquid state. The heat given out in this condensation is equal numerically to that necessary to convert 2 H^2O in the liquid state into vapor exerting in the gaseous state a pressure of 6.19 atmospheres.

The latent heat of vaporization of 1 kilo of H_2O at 0° is 606.5 calories (Regnault), or for 18 parts 10,917 calories. If we subtract the outer work done in giving tension to the vapor (2T), the work of vaporization without outer work is 10,917—546 = 10,371 calories. At 18°, by a similar calculation, the work of vaporization is (594 × 18)—2(273+18) = 10,692—582 = 10,110 calories. The outer work, however, if the vapor exerts 6.19 atmospheres pressure, is 6.19×2T = 6.19×582 = 3,590 calories. The total work of vaporization, including the work necessary to give the vapor the requisite tension of 6.19 atmospheres is 10,110 +3,590 = 13,700 calories. Therefore, combined H and OH, at a tension of 6.19 atmospheres, will give out in condensing to combined H and OH, as liquid water, at 18° C, 13,700 calories. The heat of neutralization, 13,740 calories is, therefore, nothing else than the physical heat of condensation of 18 parts of *combined* H and OH to 18 parts of liquid water.

An exactly similar conclusion follows from a thermochemical consideration of the heat of formation of an "ionized" H_2O molecule in dilute solution. The thermochemical constants of $H^{\cdot}$ and $(OH)'$ are already given in the tables, and their sum must be the heat of formation of water from hydrogen and oxygen

gases, when the molecule remains in dilute solution, *i. e.*, "ionized."

$$\begin{aligned} H^{\bullet} &= - \quad 900 \text{ calories} \\ (OH)' &= + \ 56{,}100 \quad " \\ \text{Sum} &= + \ 55{,}200 \quad " \end{aligned}$$

This represents the heat of formation in dilute solution, with the molecule "ionized" so as to exert the usual osmotic pressures of H and OH ions in the dilute solutions used. In the concrete case of mixed NaOH and HCl solutions, we have found this osmotic pressure to have been 6.17 atmospheres. To calculate what the heat of formation of the "ionized" molecule would be if it exerted 1 atmosphere pressure, we add to 55,200 the work of expansion from 6.19 atmospheres to 1 atmosphere $=(6.19-1) \times 2T = 5.19 \times 582 = 3{,}021$ calories, giving a total of 58,221 calories. But the heat of formation of *vapor of water* at 18° from oxygen and hydrogen gas is, as nearly as can be calculated from Regnault's experiments, 58,100 calories. It thence follows, that the heat of combination of hydrogen and oxygen gases to form an "ionized" molecule, in dilute solution, the ionized molecule exerting an osmotic pressure of one atmosphere, is equal to or identical with the heat of combination to form vapor of water at one atmosphere tension; from which follows the substantial identification of the "ionized" water molecule ($H^{\bullet}$ and $(OH)'$ ions at a given osmotic pressure) with the gaseous state of water vapor at the same pressure.

Two lines of reasoning and calculation therefore give proof to the thesis, that the heat of neutralization is merely the heat evolved in the condensation of a gaseous H_2O molecule into the liquid state, and this conclusion, again, agrees further with the conception that the "ionized" condition of a molecule in dilute solution is merely a certain physical condition of the compound, and that "ionization" is in no sense to be regarded as a resolution or decomposition of the molecule into its constituents. An "ionized" molecule is still a molecule of the *compound*, with its constituents still in the *combined* condition.

If it be objected that the heat of neutralization is not a constant for all acids and bases, but that there are irregularities, it has

been shown by Arrhenius that these irregularities are due to imperfect or incomplete "ionization" of either the acid or base or both, and that when this is allowed for, the irregularities disappear or are explained. Exactly the same line of reasoning would account for the irregularities, assuming the line of explanation of the heat of neutralization which has been brought forward in this paper.

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A paper read by title at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 19, 1903, President Richards in the chair.

BERTHELOT'S LAW RELATIVE TO THE ELECTROMOTIVE FORCES OF CELLS BASED ON THE RECIPROCAL ACTION OF SALINE SOLUTIONS AND SOLUBLE ELECTROLYTES.[1]

By C. J. Reed.

This law, as recently announced by Berthelot, and illustrated by examples, which he states as proofs, is as follows:

"When a base acts upon an acid, the electromotive force developed is the sum of the electromotive forces developed by the reaction of the corresponding salt separately upon the acid and upon the base. The reacting solutions are supposed to be dilute, in equivalent proportions, and to give rise to no separation of gaseous or insoluble products, and to undergo no progressive change in their internal constitution other than neutralization."

This law he illustrates by the following example: The three solutions,

HNO_3, 63 grams + Aq 5 liters,
NaOH, 40 grams + Aq 5 liters,
$NaNO_3$, 85 grams + Aq 5 liters,

are brought to a temperature of, for example, 14°. The electromotive force, E, developed by the reaction, HNO_3 + NaOH, gives 0.56 volt[2]; the electromotive force, e_1, developed by the reaction, HNO_3 + $NaNO_3$, is 0.15 volt; the electromotive force, e_2, developed by the reaction, $NaNO_3$ + NaOH, is 0.42 volt. The sum of the last two electromotive forces, 0.42 + 0.15 = 0.57 volt, is a value agreeing sensibly with the electromotive force 0.56 volt.

Berthelot considers this agreement particularly striking, for the reason that it held true of electromotive forces determined by him without prejudice, and two years prior to the discovery of his alleged law in experiments in which he used platinum electrodes and took the maximum values observed after the circuit had been

[1] Comptes Rendus, February 16, 1903.
[2] Annales de Chimie et de Physique, 7e Serie, t. xxvii.

closed a certain definite time. Berthelot makes the reservation that there must be no oxidation or reduction.

The experimental proof of this law, according to Berthelot, consisted in opposing experimentally the electromotive force developed by the action of an acid on a base, and the sum of the two electromotive forces developed by the reactions of the salt separately on the acid and on the base. He used a series of six cells, separated by porous walls. In the terminal cells of the series he placed electrodes of metallic zinc, each in contact with a concentrated solution of a salt of zinc, such as zinc sulphate. In the cells adjacent to the terminal cells he placed a neutral sodium salt of the corresponding acid. In the remaining cells he placed the solutions to be tested, viz.: the neutral salt and the acid, the neutral salt and the base, or the acid and the base.

The solutions used by Berthelot contained one monovalent gram-molecule in 5 liters of water. With the following combination he finds the electromotive force = 0:

$$(Zn)\,SO_4Zn \mid SO_4Na_2 \overset{e_1}{\frown} SO_4H_2 \mid 2NaOH \overset{E}{\frown} SO_4Zn \mid (Zn)\,\overset{e_2}{\frown}.$$

He now measures separately the electromotive force of each pair of adjacent electrolytes with platinum electrodes, obtaining the following results:

$$E = Pt \mid H_2SO_4 \mid 2NaOH \mid Pt = 0.62 \text{ volt.}$$
$$e_1 = Pt \mid Na_2SO_4 \mid H_2SO_4 \mid Pt = 0.24 \text{ volt.}$$
$$e_2 = Pt \mid 2NaOH \mid Na_2SO_4 \mid Pt = 0.405 \text{ volt.}$$

As the sum of e_1 and e_2 is sensibly equal to E, he considers this a verification of his law with polarizable platinum electrodes.

As a corroboration of this, he assumes that the same result should be obtained by either of the two following combinations with platinum electrodes:

$$E = Pt \mid H_2SO_4 \mid 2NaOH \mid Pt$$
$$e_1 + e_2 = Pt \mid H_2SO_4 \mid 2NaOH \mid Pt$$

The experimental result in this corroboration gives:

$$E = 0.63 \text{ volt},$$
$$e_1 = 0.24 \text{ volt},$$
$$e_2 = 0.40 \text{ volt},$$

the sum of $e_1 + e_2$ being 0.64.

He gives the results obtained in this manner with various combinations of electrolytes, including sodium hydrate, ammonium, hydrate, sulphuric acid, hydrochloric acid, nitric acid, boracic acid, formic acid, acetic acid, oxalic acid and lactic acid.

In all cases the chain of electrolytes terminating in zinc electrodes in contact with a neutral zinc salt (unpolarizable) gave sensibly no electromotive force. This forms the basis of his assumption that the sum of the electromotive forces in this chain is equal to 0. So far as these experiments alone are concerned, they prove nothing, except that an electrolytic chain terminating in similar electrodes, making contact with similar solutions, gives no electromotive force. All of his numerical values rest upon the experiments made with platinum electrodes, and in all of these cases the acid is in contact with one platinum electrode and in contact with an alkaline or a neutral solution, which in turn is in contact either with the other electrode or with an intervening electrolyte. The alkaline solution is in contact with one electrode and with an acid or neutral solution, which in turn is in contact either with the other electrode or with an intervening electrolyte. But in all cases the only electromotive forces which Berthelot considers are the zero electromotive forces (uniformly obtained when unpolarizable electrodes are used), and the electromotive forces measured between platinum electrodes in contact with different solutions.

If we examine Berthelot's experimental proof as to the equality of E and $e_1 + e_2$, we find that there is no proof. There is, in fact, no proof of the existence of any electromotive forces, E, e_1 and e_2, between the solutions, all measurements of these quantities having been made between platinum plates in contact with different solutions. There is no proof that these electromotive forces were developed at the junctions of two solutions. They may, with at least equal probability, have been developed at the junctions of the electrodes with the two different solutions, and this seems to me the most reasonable supposition. We know that, in general, electrochemical electromotive forces are developed at the junctions of electrodes with electrolytes. We know this from the development and absorption of energy at those surfaces. There is, on the other hand, no experimental proof of the existence of an

electromotive force at the junction of two electrolytes. Such a junction cannot even be a definite surface of separation.

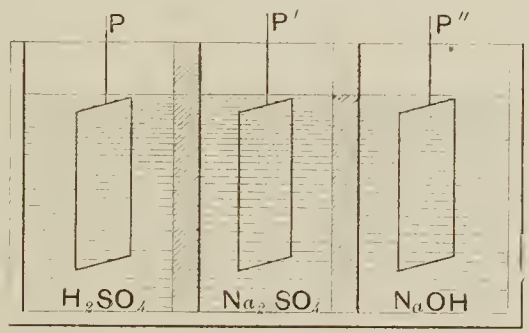
Berthelot appears to have overlooked the fact that in attempting to measure the electromotive force of the combination, Pt | H_2SO_4 | 2NaOH | Pt, he actually measured the electromotive force of the combination, Pt | H_2SO_4 | Na_2SO_4 | 2NaOH | Pt, since it would not be possible to bring H_2SO_4 and NaOH in direct electrolytic contact without neutralization taking place along the entire surface of juncture, and forming instantly a layer of Na_2SO_4. In the experiment he describes this layer would, of course, be thin and probably contained within the porous wall, but it would nevertheless form as perfect a separation between the H_2SO_4 and the NaOH as in the case in which he inserts beforehand a considerable quantity of Na_2SO_4. The two experiments, therefore, amount merely to a repetition of the same experiment. The fact that he obtained 0.63 volt in the one experiment and 0.64 volt in the other is neither a remarkable circumstance nor one from which his conclusions could be deduced.

The only experiments of Berthelot from which any conclusion can be drawn are those in which the electromotive force was measured between platinum electrodes, one in contact with an acid and one in contact with a base (the acid and base being separated by the neutral salt); and those in which the electromotive force was measured between platinum electrodes, one in contact with a neutral salt and the other in contact with either the acid or the base of the salt. These experiments are interesting, and are in agreement substantially with the law as stated by Berthelot, but they are also in equal agreement with another law, which I shall propose in place of that proposed by Berthelot, as it appears to me to be a more direct inference from the experimental proofs which he has adduced. There is also no experimental proof either in these experiments described by Berthelot or in any experiments which I have been able to find anywhere on record of the existence of an electromotive force at the junction of dissimilar electrolytes. All alleged measurements of such electromotive forces have been made, not between elctrolytes, but between electrodes in contact, either directly with the liquids assumed to be measured or by the intervention of some other electrolyte.

The law which I propose as a substitute for that of Berthelot, and which agrees in every respect with his experiments, is as follows:

"When a base acts upon an acid, the electromotive force developed is zero. When a salt acts upon the corresponding acid or the corresponding base, the electromotive force developed is also zero. The electromotive force at the junction of two electrolytes, whether chemical reaction takes place or not, is zero under all circumstances. The electromotive force between a platinum plate and an acid, and the electromotive force between a platinum plate and a base measured separately, equals the sum of these electromotive forces measured simultaneously."

I would suggest the following form of experiment (somewhat simpler than Berthelot's), which will serve as a proof of this law in all cases: Three electrolytes are placed in series, separated by porous partitions, each containing a platinum electrode. Into one terminal cell is placed the acid, into the other terminal cell is placed the base or alkali and into the intermediate cell the corresponding salt. In all cases the sum of the electromotive forces measured between two adjacent electrodes should equal the electromotive force between the extreme electrodes, provided no current is allowed to pass which is sufficiently great to chemically change the platinum electrodes or the solution before all measurements have been made. The subjoined figure shows this arrangement. P, P′ and P″ represent platinum electrodes in H_2SO_4, Na_2SO_4 and NaOH, respectively. The electromotive force between P and P″ should equal that between P and P′ added to that between P′ and P″.



An inspection of the cells in which Berthelot found a measureable electromotive force shows them all to be concentration cells,

and shows that the only sources of electromotive force are the differences in the concentration of an electrolyte at the two electrodes, the chemical energy of the reaction between the acid and the base having no effect whatever.

The law, as stated by me, simply means that the electromotive force of a concentration cell, consisting of platinum electrodes and one electrolyte of different concentrations, is not altered by the presence in solution of other electrolytes.

Let us suppose that, with the three substances used by Berthelot, $\frac{n}{10}$ H_2SO_4, $\frac{n}{10}$ Na_2SO_4 and $\frac{n}{5}$ NaOH, we form three concentration cells having platinum electrodes, one electrode in each being immersed in water and the other electrode in one of these solutions. We obtain the following:

$$\text{Pt} \mid \text{Aq} \mid \tfrac{n}{10}\ H_2SO_4, \text{Aq} \mid \text{Pt} \ldots\ldots\ldots\ldots\ldots\ldots (1).$$
$$\text{Pt} \mid \text{Aq} \mid \tfrac{n}{10}\ Na_2SO_4, \text{Aq} \mid \text{Pt} \ldots\ldots\ldots\ldots\ldots\ldots (2).$$
$$\text{Pt} \mid \text{Aq} \mid \tfrac{n}{5}\ \text{NaOH}, \text{Aq} \mid \text{Pt} \ldots\ldots\ldots\ldots\ldots\ldots (3).$$

In these cells the concentration of the solute in the left-hand compartment is zero.

Let the unknown electromotive forces of these cells be represented respectively by a, b and c.

Now, suppose that any two of these cells may be combined into one by merely adding the contents of the cells without changes of concentrations, and suppose that this union produces no change in the individual electromotive forces. We then have, by combining (1) and —(2),

$$\text{Pt} \mid \tfrac{n}{10}\ Na_2SO_4, \text{Aq} \mid \tfrac{n}{10}\ H_2SO_4, \text{Aq} \mid \text{Pt},$$

the electromotive force of which is a—b. This, as measured by Berthelot, is 0.24 volt.

In this cell the concentration of the H_2SO_4 in the left-hand compartment is still zero, as is also the concentration of Na_2SO_4 in the right-hand compartment. In other words, the osmotic pressure of H_2SO_4 towards Na_2SO_4 solution must be the same as towards water, and the osmotic pressure of Na_2SO_4 towards H_2SO_4 solution is the same as towards water. It is assumed, of course, that we are dealing with H_2SO_4 and Na_2SO_4 molecules, not with their constituent parts or ions.

Similarly combining (2) and —(3), we have

$$Pt \mid \tfrac{n}{5}\ NaOH, Aq \mid \tfrac{n}{10}\ Na_2SO_4, Aq \mid Pt,$$

the electromotive force of which is b—c, and this, according to Berthelot, is 0.405 volt.

By combining in a similar manner (a—b) + (b—c), we obtain a—c, which is

$$Pt \mid \tfrac{n}{5}\ NaOH, + \tfrac{n}{10}\ Na_2SO_4, Aq \mid \tfrac{n}{10}\ H_2SO_4 + \tfrac{n}{10}\ Na_2SO_4, Aq \mid Pt.$$

The electromotive force of this combination should be 0.24 + 0.405 = 0.645, and this agrees with the measurements of Berthelot.

The same reasoning applies with exactly the same force to all the other experiments of Berthelot, showing that the electromotive forces which he measured are merely those of concentration, and not those of chemical reaction.

Reasoning also *a priori,* why should we expect an electrochemical electromotive force to result from the junction of a salt with its acid or its base, since no chemical action or change results from such a junction?

In all of the cells investigated by Berthelot, in which he particularly eliminates by hypothesis any oxidation or reduction, the chemical changes produce no changes of valence, no liberation or formation of ions according to Faraday's law, and, therefore, no electrochemical action. If the only chemical change which occurs in the cell is not electrochemical, the energy of that chemical change cannot be a source of electromotive force.

Berthelot's observations are, therefore, only what would necessarily follow if these cells be considered merely as concentration cells and the solutes be considered to be in the condition of *molecules* instead of *ions.*

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 19, 1903, President Richards in the Chair.

THEORETICAL PROPERTIES OF FREE IONS IN SOLUTIONS.

By E. F. Roeber

The following paper is intended to be an introduction to the general discussion of the electrolytic dissociation theory which is on the programme for this morning. A general discussion, in order to be successful, requires that all who take part agree with each other concerning the meaning of the terms which are used. Otherwise endless confusion and continuous misunderstanding are unavoidable. This danger is especially great in the case of the electrolytic dissociation theory which, when first placed before the scientific world by its enthusiastic and impetuous promoters, was pronounced in somewhat aggressive terms, which could be misunderstood when taken verbatim.

The terms of a theory are often based on analogies of the facts to be described with other well-known facts. For instance, we say that an electric current flows through a circuit from higher potential to lower potential; and what flows through the cross-section of the circuit in unit of time, we call quantity of electricity. This terminology is based on certain analogies of the phenomena of an electric current in a circuit with the well-known phenomena of a liquid flowing in a pipe from a higher level to a lower level. The equations which represent certain phenomena of an electric current are exactly the same as the equations representing certain phenomena of the flow of a liquid through a pipe. Everybody is familiar with the latter phenomenon; hence, in order to familiarize ourselves with the phenomena of the electric current, it is useful to illustrate them by the analogy with the flowing water and to emphasize this analogy by using a similar terminology in both cases. But nobody means to say that the phenomena are the same in both cases. Nobody claims by any means that in an electric circuit something like a fluid is really flowing.

While the use of a similar terminology based on certain

analogies between different classes of phenomena has become universal in physics, it appears that grave objections are sometimes raised against the same practice in the case of the electrolytic dissociation theory. Objections are raised when we speak of electrolytic dissociation, for the reason that it is not chemical dissociation, or when we speak of free ions, for the reason that they are not free in every respect. But it seems to me that the electrolytic dissociation theory only follows common practice which has been found extremely useful in all different fields of physical science; and, to justify this standpoint, I wish to quote some sentences from Maxwell.* For two reasons, first, because, to my knowledge, the importance of the use of models and physical analogies for the progress of science has nowhere been so clearly pointed out as in these sentences of Maxwell; second, because these sentences are taken from the introduction of those papers which probably represent the greatest triumph of the use of physical analogies, the fundamental equations of the modern theory of electromagnetism being developed with the aid of such analogies.

"The first process in the effectual study of the science, must be one of simplification and reduction of the results of previous investigation to a form in which the mind can grasp them. The results of this simplification may take the form of a purely mathematical formula or of a physical hypothesis. In the first case we entirely lose sight of the phenomena to be explained; and though we may trace out the consequences of given laws we can never obtain more extended views of the connection of the subject. If, on the other hand, we adopt a physical hypothesis, we see the phenomena only through a medium, and are liable to that blindness to facts and rashness in assumption, which a partial explanation encourages. We must, therefore, discover some method of investigation which allows the mind at any step to lay hold of a clear physical conception, without being committed to any theory founded on the physical science from which that conception is borrowed, so that it is neither drawn aside from the subject in pursuit of analytical subtleties nor carried beyond the truth by a favorite hypothesis. In order to obtain physical ideas without adopting a physical theory, we must make ourselves

* Maxwell, On Faraday's Lines of Force (1855), Scientific Papers, vol. I, p. 155.

familiar with the existence of physical analogies. By a physical analogy, I mean that practical similarity between the laws of one science and those of another, which makes each of them illustrate the other."

By the use of analogies of this kind, Maxwell says, we bring before the mind in a convenient and manageable form those mathematical ideas which are necessary to the study of the phenomena. By stripping an analogy of its physical dress and reducing it to mathematical formulas, we obtain "a system of truth, strictly founded on observation, but probably deficient both in the vividness of its conceptions and the fertility of its methods." For his purpose, Maxwell refers everything to the purely geometrical idea of the motion of an imaginary fluid to which he attributes certain properties.

I have referred to Maxwell somewhat at length, because I think the theory of free ions in solution should be considered from a similar point of view. The main result of the whole theory of free ions is, in my opinion, that it gives us a mechanical model which illustrates electrolytic phenomena in solutions, that it resolves the electrolytic phenomena into a mechanics of ions, that it is a simple scheme enabling us to prophesy what will happen in a given solution under given conditions.

As all electrolytic phenomena are to be illustrated by motions of free ions, it becomes all important to state clearly the properties which we attribute to these free ions. For this purpose it may be useful to give a brief summary of the facts as they are and of the way by which they are illustrated by the model of traveling ions. By stripping the illustration of all unnecessary dress, we can deduce the properties of free ions in naked simplicity.

Some fundamental facts of electrolysis are stated in Faraday's law, which gives the quantity of material changed in chemical constitution by the passage of the current, as function of the number of coulombs which have passed. The chemical change invariably consists of reduction at the cathode and oxidation (or "perduction") at the anode. If n is the change of valency of the element reduced at the cathode or of the element oxidized at the anode (or, to use Prof. Otis C. Johnson's well-known notation of bonds, if n is the number of positive bonds lost or

gained by one atom at the cathode or anode respectively), then the quantity of the element reduced or oxidized by the passage of a ampères for t seconds is $\frac{0.0000104}{n} at$ gram atoms.

This statement of Faraday's law has the advantage of stating the facts completely and briefly, but it is, at least to my mind, somewhat unsatisfactory for practical use, because it is deficient in the vividness of its conceptions. Faraday himself has indicated how to overcome this deficiency and how to illustrate these facts by the mechanical model of traveling ions. By dividing each molecule of the electrolyte into an anion and a cation and assuming a relative motion of the cations against the anions—either a motion of the cations towards the cathode or of the anions towards the anode or both simultaneously—we evidently get a mechanical model illustrating the fact that in the interior of a uniform electrolyte there is no chemical change, while the relative motion of the two kinds of ions yields us at the electrodes a number of free cations and anions ready to undergo reduction and oxidation respectively. Reduction of an element represents a decrease of valency, or, in Prof. Johnson's notation, a loss of positive bonds or a gain of negative bonds. Oxidation of an element represents an increase of valency, or, in Prof. Johnson's notation, a gain of positive bonds or a loss of negative bonds. Now, this oxidation and reduction is combined in electrolysis with the passage of coulombs through the system, and we arrive at a complete statement of Faraday's law if we assume that in our mechanical model the traveling ions transport the coulombs through the electrolyte, and that each bond in Johnson's notation corresponds to a charge of $1 \div 0.0000104$ or 96,600 coulombs, each positive bond to 96,600 positive coulombs, each negative bond to 96,600 negative coulombs. Our mechanical model of traveling ions thus serves to represent the two apparently different, although always combined, phenomena of the transport of electricity through the system and of the chemical oxidation and reduction at the electrodes, as one and the same phenomenon. When c coulombs pass through the system from the anode to the cathode, then our model of migrating ions must yield us at the anode $\frac{0.0000104\,c}{n_1}$ free gramions, each of which gains n_1 positive bonds or $96{,}600 n_1$ positive coulombs, hence all these gramions together receive c coulombs from the anode. Simultaneously

$\frac{0.0000104\,c}{n_2}$ gramions undergo reduction at the cathode, each losing n_2 positive bonds or $96{,}600n_2$ positive coulombs, so that all these ions together give off c coulombs to the cathode.

I have distinguished here n_1 and n_2 for the reason that in the general case the change of valency of one atom at the anode will be different from the change of valency of one atom at the cathode; c is, of course, the same in both cases. Hence, in the general case we will not have the same number of gramions oxidized at the anode as reduced at the cathode. For every $\frac{0.0000104\,c}{n_1}$ gramions oxidized at the anode we have $\frac{0.0000104\,c}{n_2}$ gramions reduced at the cathode; or for every n_2 gramions oxidized at the anode we have n_1 gramions reduced at the cathode. This is Johnson's well-known rule* for balancing equations, which represent oxidation and reduction; for electrolytic oxidation and reduction this rule thus is a direct consequence of Faraday's law.

From Faraday's law we, therefore, derive one—and the most important, because universal—property of ions: that each ion is electrically charged, the charge of each gramion being equal to 96,600 coulombs times the number of bonds in Johnson's notation. Thus in $CuSO_4$, according to Johnson, Cu has 2 positive bonds, S has 6 positive bonds and O_4 has 8 negative bonds; hence, if the ions are Cu and SO_4, then each gramion Cu is charged with 2 x 96,600 coulombs of positive electricity, each gramion SO_4 with 2 x 96,600 coulombs of negative electricity.

Concerning the nature of this electric charge I emphasize that we are absolutely at liberty to stipulate it, in order to make our model agree with the facts. I emphasize this on account of some critical remarks made by Mr. C. J. Reed in a communicated discussion of Dr. L. A. Parson's paper in the third volume of the Transactions of our Society (page 278). Mr. Reed claims that the adherents of the dissociation theory must assume that these charges are ordinary charges, and that the change of an ion into an atom must always represent an evolution of energy. Mr. Reed says that if the adherents of the dissociation theory don't accept this and argue otherwise, then their electric charges of the ions are not electric charges, but mysteries. Mr. Reed asks: If mystery alone is an all-sufficient theory, why should we labor to build a theory, consisting of only one part mystery and five

* Prescott and Johnson, Qualitative Chemical Analysis.

parts mathematics, which contradicts itself and then does not account for the facts?

While I greatly enjoy Mr. Reed's straightforward and impetuous argument, it seems to me that he absolutely misunderstands the value and purpose of mechanical models and of physical analogies. I like to refer again to Maxwell. Maxwell wants to illustrate electromagnetic phenomena by their analogy with the behavior of an incompressible fluid moving in certain unit tubes. To this imaginary incompressible fluid he attributes those properties which suit his purpose. For certain cases he must assume that in the space under consideration there are sources capable of creating and emitting his incompressible fluid, and that at other places there are sinks capable of receiving and destroying his incompressible fluid. Now, first to assume an incompressible fluid, and then to assume that at certain places it can be created from nothing or can be annihilated, would be, from Mr. Reed's standpoint, nonsense in itself. But Maxwell says: "There is nothing self-contradictory in the conception of these sources where the fluid is created, and sinks where it is annihilated. The properties of the fluid are at our disposal; we have made it incompressible, and now we suppose it produced from nothing at certain points and reduced to nothing at others."

In the same way, the adherents of the dissociation theory have all the properties of ions at their disposal. From Faraday's law it only follows that each gramion has a charge equal to a multiple of 96,600 coulombs; but Faraday's law says nothing concerning the connection between the ion and its charge. As far as we have gone, the assumption of charged ions is only a way of stating Faraday's law in a convenient way. Now, as Faraday's law has absolutely nothing to do with the energy changes in electrochemical action, it is a priori evident that as long as our model of migrating ions serves only to illustrate Faraday's law, we cannot say anything concerning the energy changes involved in the change of an ion to an atom.

Moreover, it is at once clear that there must be an essential difference between ordinary electric charges and the electric charges of ions. If you have a metallic globe you may charge it to any potential, you may put on it as many coulombs as you please. But this is not the case with ions; each gramion has a

distinct charge, not more and not less; and these electric charges combine with the atoms or radicle in multiple proportions, according to Faraday's law. This leads us at once a step further. We may argue, according to Nernst, that as the law of the combination of chemical elements by multiple proportions has led to the mechanical picture of the atomic theory, in the same way we may be led by Faraday's law to assume somewhat like an atomic theory of electricity. According to our model of Faraday's law, any gramion of any kind is charged with a multiple of 96,600 coulombs of positive or of negative electricity; we may, therefore, assume two new kinds of atoms, electric atoms or—as we now call it—electrons, a positive electron always having a positive charge of 96,600 coulombs, and a negative electron a negative charge of 96,600 coulombs. The mass of these electrons must be assumed so small that, for all chemical purposes, it is negligible compared with the mass of the atoms of the ordinary chemical elements.

Ions are then saturated compounds of atoms and electrons. If Cu and SO_4 are the ions of $CuSO_4$, then the cation Cu is to be considered as the compound of an atom Cu with two positive electrons, and the anion SO_4 as the compound of the chemical radicle SO_4, with two negative electrons. It is then at once clear that the ion Cu is essentially different from the atom Cu, and that the adherents of the ionic theory are in no way compelled to concede the correctness of the basis of Mr. Reed's criticism, namely, that the change from an ion into an atom should always evolve energy. If we do not take other facts into account we cannot say anything concerning the energy change involved in the change of Cu from the ionic to the atomic state. But if we take other facts into account, we can make this energy change in our model suit the facts, and then our model is just as good an illustration of the facts as any other theory.

But I digress. As I have pointed out the only properties which we have to attribute to ions in order to suit Faraday's law are that every gramion is charged with a multiple of 96,600 positive or negative coulombs, and that the ions travel under the influence of a drop of electric potential, either the cations towards the cathode, or the anions towards the anode, or both simultaneously.

From conductivity measurements we can find what the relative speed is with which the cations travel against the anions under

the influence of a given e. m. f., or in other words we can determine the sum of the cations and anions passing through a cross-section of the circuit in a given time in opposite directions. But we cannot determine the absolute velocity with which the cations alone travel and the anions alone travel, or the number of cations passing a cross-section of the circuit in one direction and the number of anions passing it in the opposite direction. To suit only the facts expressed in Faraday's law, we might just as well assume that only the cations travel or only the anions travel, or we may assume the ratio of the speeds of the cations and anions to be anything we like.

Further, from the fact expressed in Faraday's law alone we cannot even say what the ions are. For example in the case of the lead accumulator, if we only want to know how many grams of lead peroxide and spongy lead are theoretically required to give so and so many ampère hours, we may make use of the old-fashioned idea that the hydrogen and oxygen of the water constitute the ions, that the hydrogen ions arriving at the cathode and the oxygen ions arriving at the anode change the lead peroxide and the spongy lead into PbO, and that the PbO is changed by the sulphuric acid into $PbSO_4$. The result, giving the grams of Pb and PbO_2 consumed and of $PbSO_4$ produced per ampère hour, is in this calculation exactly the same as if we assume, according to modern views, that H ions and SO_4 ions transport the electricity through the solution.

Moreover, from Faraday's law alone we cannot even say when a certain metal is deposited on the cathode as the result of the passage of an electric current that this metal represents the cation traveling towards the cathode. I may refer to the familiar example of the deposition of gold from a cyanide solution. From a $KAuCy_2$ solution we get at the cathode, a deposit of gold, but this does not prove that Au is the positive ion and KCy_2 the negative ion. In fact, we now know that K and $AuCy_2$ are the ions, that potassium is primarily (electrochemically) deposited on the cathode, and that the potassium reacts with the $KAuCy_2$ in the solution so that the gold deposit is really a secondary product.

It is thus clear that from Faraday's law alone we get but a very limited model of migrating ions. To complete our model,

we must take other facts into account. The principal deficiency of our model, so far developed, is that in a given case we do not know what are the ions and what are the absolute velocities with which we must assume our ions to travel. The credit for having discovered the means of answering these questions is due to Hittorf.

If we work out our model of anions and cations migrating in different directions in a solution, we find that the reduction and oxidation at the electrodes are not the only changes taking place, but that concentration changes in the solution itself near the anode and near the cathode must necessarily result. These concentration changes as calculated from our model will be entirely different if we divide a molecule of the electrolyte in different ways into an anion and a cation; this is quite evident in the case of the cyanide solution, previously referred to; it was in this way that it was shown that K, not Au must be the cation in a $KAuCy_2$ solution. Moreover, if we have found what the ions are, measurements of the concentration changes in the solution near the electrodes enable us to calculate the ratio of the two velocities with which the cations migrate in one direction and the anions in the opposite direction.

The conductivity measurements give the sum of the velocities with which both kinds of ions travel under a given electromotive force. Hence, Kohlrausch, by combining the sum of the velocities, as determined by himself, with their ratio, as determined by Hittorf, could determine the absolute velocity of each kind of ion and thereby found the fundamental law that in an infinitely dilute aqueous solution the mobility of a certain kind of ion is a characteristic constant of this kind of ion and is independent of the other kinds of ions present in the solution. For instance, the mobility of H ions is always the same whatever may be the nature of the acid; and the mobility of Cl ions is always the same whatever may be the chloride.

The mobility is the velocity with which the ion travels under the influence of a drop of potential per unit length, equal to one dyne. Kohlrausch's *Beweglichkeit* is, therefore, not a velocity, and has not the dimensions of a velocity. We get the velocity of an ion when we multiply the *Beweglichkeit* with the mechanical force acting on it. To avoid misunderstandings, the term mobil-

ity, instead of velocity, seems, therefore, greatly preferable for Kohlrausch's Beweglichkeit. But this is only an incidental remark. The fundamental point is that the mobility of an ion is a new property, characteristic for each kind of ion in an infinitely dilute aqueous solution.

Our model thus becomes complete for infinitely dilute aqueous solutions of uniform concentration. Electrolytic action in such solutions is produced by the migrations of ions which have two characteristic properties: each ion carries a distinct electric charge and each ion travels with a distinct velocity, equal to its mobility multiplied with the force acting on it in mechanical measure. There is, however, one important difference between these two properties of ions: the electric charge is a universal property of any ion in any electrolyte, while the mobility is proven to be a constant quantity so far only for infinitely dilute aqueous solutions. But if we restrict for the present our considerations to the latter, then our mechanical model is complete. It gives us a complete illustration of what takes place: of the oxidation and reduction at the electrodes and of the concentration changes in the solution. And as far as it goes, it is nothing but a statement of facts, there is nothing hypothetical in it.

But what does it mean that in such an infinitely dilute solution each ion travels with a mobility absolutely independent of the other ions present in the solution? To my mind, the term "free ion" is a very useful and expressive term for this property. It means that a Na ion in its movements in the electrolyte—which in our model represent all the changes going on—is independent of the other ions; if the force is the same, the velocity of the Na ion is the same whether we have a solution of NaCl or NaOH. We say Na is free from Cl or free from OH, and this freedom means nothing but what we have stated above, as a consequence of Kohlrausch's law.

Nobody has ever claimed that the Na ion is free like an atom in a dissociated gas; nor would it be right to say that the Na ion is free from the water. We do not know anything about that. The mobility depends certainly upon the solvent, and it is quite possible that even in an infinitely dilute solution the Na ion while migrating is combined in some way with the solvent. We do not know whether it is so or how it is, but as stated before for practical purposes our model is complete.

As far as I can see, these properties of free ions are all that is claimed by the dissociation theory for infinitely dilute aqueous solutions, with the exception of some properties which are sometimes assumed in a more qualitative way, like color and certain physiological properties of ions. As these assumptions have not found any exact mathematical formulation, I will not discuss them here.

The application of the dissociation theory to analytical chemistry has led to the claim that it is always between ions that the instantaneous chemical reactions take place in a solution. On account of this application, the dissociation theory appears in a new light and becomes of great interest to the pure analytical chemist. But new properties are not attributed to the ions for this purpose. In this connection it is only fair to refer to Kahlenberg's well-known experiments on instantaneous chemical reactions in non-electrolytes, which, to my mind, appear to indicate the danger of unproven generalizations. While the facts appear to show a connection between chemical affinity and degree of electrical ionization in aqueous solutions, it is very dangerous, as Kahlenberg has shown, to apply this view without further proof to other solutions than those for which it has been found to hold true.

A few words may be said concerning thermodynamics and the ionic theory. I want to emphasize that by purely thermodynamical reasoning we can never find new properties of ions. This is really self-evident. To apply the principles of thermodynamics to dilute solutions, we must make distinct assumptions concerning a dilute solution. For instance, we assume the energy* of a dilute solution to be a linear function of the numbers of the different molecules contained in the solution. This assumption is mathematically reasonable, if we develop the function which represents the energy, in form of a series of Taylor, and then introduce the mathematical simplification due to the relatively large number of the molecules of the solvent compared with those of the dissolved substances. Then the energy becomes a linear function of the numbers of the molecules of the different substances. But this mathematical simplification has a distinct physical meaning, namely, that the energy of a dilute solution is independent of the

* M. Planck, Vorlesungen über Thermodynamik, page 211.

mutual action of the dissolved substances between each other. Similar remarks may be made concerning the functions representing the volume and the entropy of a dilute solution. Thus the fundamental functions on which we build up the thermodynamical theory of dilute solutions already contain distinct physical assumptions on the properties of such solutions. It seems superfluous to say that with these remarks I do not wish to belittle in the least the splendid achievements attained by thermodynamical methods in the modern development of the theory of solutions. Thermodynamics has served the extremely useful purpose of systematizing the whole theory, of connecting different fields with each other, of supporting one part by another.

The most important achievement of the thermodynamic theory of solutions is the partial parallelism between the theory of dilute solutions and the theory of gases. This parallelism is based on the experimental fact that the osmotic pressure in a solution obeys the gas laws. This fact enables us to extend our model of free ions which we found to be an illustration of uniformly concentrated dilute solutions, now to the more general case of a system of not uniform concentration. Nernst's theory of diffusion and his theory of concentration cells represent this generalization; they are probably one of the boldest and most successful attempts in the history of science of generalizing a model which had been found useful in a restricted field, so as to apply to a much broader field. Simplicity is the keynote of Nernst's theory. He follows exactly the lines of the model as laid out before for uniform solutions. Whatever happens in a system of solutions, is described as the result of a motion of ions. Each ion moves with a velocity, equal to its mobility multiplied with the force acting on it. This force is the resultant of two different kinds of forces: the electric forces due to the electric charges of the ions, and the osmotic forces due to the difference of osmotic pressure, or, in other words, due to the differences of concentration. The electric forces act against the osmotic forces and equilibrium exists when both forces balance each other at each point in the solution. These are absolutely all assumptions which Nernst makes for the interior of an electrolyte, and the complete success of his theory of diffusion and concentration cells represents the proof of the usefulness of our model. The only essentially new

conception introduced by Nernst into the model of ions, is the solution tension at the boundary surface of a reversible electrode and the electrolyte. But the solution tension is a property of both electrode and electrolyte, and expresses rather the boundary condition of our model at the junction of electrolyte and electrode, than a property of the ions in solution; for this reason I need not discuss it here.

That the above-mentioned assumptions represent, indeed, the complete foundation of Nernst's theory, is best seen from the way in which this theory has been formulated and further extended by Planck,* who proceeds in the following manner: If R is the osmotic pressure of 1 gramion in unit volume (R being a constant, independent of the nature of the ion), p, the osmotic pressure, φ the potential function of the total free electricity, ϵ the electric charge of a univalent gramion, then the total force acting on one ion in the direction n is

$$-\frac{R}{p}\frac{\delta p}{\delta n} - \epsilon\frac{\delta \varphi}{\delta n}$$

The first term represents the osmotic force, the second the electric force. The velocity with which an ion travels in the direction n is equal to the total force acting on it in the direction n, multiplied by its mobility. From this starting point, Planck arrives at a complete system of differential equations, which completely determine the conditions in the interior of the solution. Nernst's theories of diffusion and of concentration cells represent special applications of Planck's general system of equations.

This formulation of the theory in form of a system of general equations has one important advantage. There cannot possibly be any misunderstanding concerning its meaning, and the equations must be either right or wrong. The only way to decide this, is to draw all possible conclusions from these equations and to see whether these conclusions agree with the facts. Now, as long as experimental investigations have been restricted to very dilute solutions, all the conclusions of the theory have been found to be in agreement with the facts.

Planck's general system of equations may be considered as a statement of the ionic theory in naked simplicity, with its unneces-

* Wiedemann's Annalen, vol. 39, (1890), page 165.

sary dress removed. On the other hand the fact remains that these equations were developed on the foundation of the model of traveling ions and that this model is still the only one by which Planck's system of equations may be illustrated. To sum up, for very dilute solutions the model of the ionic theory is complete, and for dilute aqueous solutions the first discrepancy between model and facts is still to be found. We are thus justified in saying that for infinitely dilute aqueous solutions our model of ions represents a true and complete description of the facts.

But the situation changes when we pass from infinitely dilute solutions to more concentrated solutions. Arrhenius assumes that here our model still holds good if we assume that only a part of the dissolved molecules is ionized. Only these ions are active and the non-ionized molecules of the dissolved substance, as well as the molecules of the solvent, are inactive. To the active ions Arrhenius attributes the same properties as in infinitely dilute solutions, *i. e.,* he assumes that both the electric charge *and the mobility* of each ion remain the same. These assumptions represent again a model. But the trouble is that we can no longer say that this model represents the facts correctly. I may simply refer to the numerous papers of Kahlenberg.

The trouble seems to me to be right at the fundamental point of the model. If Arrhenius' model is to be used, the first thing necessary is to find an exact method of measuring the degree of ionization, *i. e.,* the ratio of the ionized molecules to the total number of dissolved molecules. According to Arrhenius' model, we should have several methods of measuring the degree of ionization, but in many cases the results of the different methods don't agree together. Hence the battle royal between Arrhenius, Jahn, Nernst and Planck, on the question which method is the right one. This situation seems, in my opinion, to indicate an inherent weakness in the fundamental conception of Arrhenius' model.

While we must admit this, it is only fair to say that even for more concentrated solutions Arrhenius' model represents an approximation of the truth, and has proven very useful in many respects, but for concentrated solutions Arrhenius' model cannot be considered to represent the facts to such a degree of completeness and truth as is found to be the case for infinitely dilute solutions.

But this is no reason to sneer at the theory. We know our model to be correct for a very special case, and we must be satisfied with the situation for the present, although in practice we have little to do with infinitely dilute solutions. But is it not similar in alternating-current engineering, where the whole theory is based on the assumption of pure sine waves, which we scarcely have in practice? Theories are tools, and as long as we have no absolutely perfect tool we must use the tools we have, and it would be foolish to depreciate the usefulness of a tool because it is not perfect.

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 19, 1903, President Richards in the Chair.

PRESENT STATUS OF THE ELECTROLYTIC DISSOCIATION THEORY.

By Wilder D. Bancroft.

The electrolytic dissociation theory consists of the assumptions that certain substances are dissociated into positively and negatively-charged ions, that these free ions carry the current in electrolytic conduction, and that they behave as separate substances. These assumptions have enabled us to account for the change of the conductivity with dilution, for abnormal molecular weights, for many cases of mass action and reaction velocity, for solubility relations, for the color of solutions, for the index of refraction, for the rotation of the plane of polarized light, for volume relations, for the taste of solutions, for toxic action, for diffusion, for electromotive forces, etc., etc. The results are consistent and more or less quantitative in nature. As a consequence the electrolytic dissociation theory has carried the chemical world by storm. It is not too much to say that those who have never accepted the theory no longer exert an effective opposition. Every day, however, it becomes clearer that the early adherents of the theory are now working along two diverging lines. One group of men has been interested in increasing the number of facts to which the theory applies. These men have been very successful. They have found what they sought, and they are more impressed than ever with the superlative excellence of the electrolytic dissociation theory. Other men, prominent among whom is Kahlenberg, have felt that the interesting things about a theory are its limitations. They also have been successful, and we now know a good deal about the shortcomings of the electrolytic dissociation theory. The agreement between the dissociation as calculated from the conductivity and that calculated from the molecular weight determinations holds only for infinitely dilute solutions. As the migration velocities change with the concentration, it is

impossible to calculate the actual dissociation for any finite concentration. The color phenomena present serious difficulties when studied carefully. Solutions of acid salts are much sourer to the taste than they should be, and their toxic action is abnormal. The change of solubility with the concentration is not what it should be and the solubility product is only an approximation. The theory of electromotive forces applies quantitatively to infinitely dilute solutions only. When solvents other than water are taken, the electrolytic dissociation theory in its present form can only be applied in the crudest, qualitative way, if at all. The final result is that the electrolytic dissociation theory applies only to infinitely dilute aqueous solutions, which is much the same as excluding the whole of actual chemistry.

Granted all this, what are we to do about it? Are we to modify the electrolytic dissociation theory or are we to substitute another theory for it; and if so, what? Kahlenberg believes that we can explain all the facts by means of the affinity between solvent and solute. While this may be true, his views are not yet sufficiently defined to constitute a theory. The same may be said of other suggestions, which have been made. Since a theory can only be displaced by another theory, the electrolytic dissociation theory will hold the field until a better one is brought forward. There is a good deal to be said in favor of the view that a modification of the present theory will be the outcome. Every one will admit that the advocates of the electrolytic dissociation theory have gone too far. They have laid too little stress on the effects due to the undissociated salt. They have been so carried away by the analogy between a solution and a gas that they have rather overlooked the analogy between a solution and a liquid. When these and other points have been taken into account, it may be that we shall have a dissociation theory which describes the facts.

But since the electrolytic dissociation theory was devised in order to account for the abnormal molecular weights of salts in aqueous solution, it may be well to ask whether there are any such abnormal molecular weights. Ramsay found that sodium, calcium and barium apparently have abnormally low molecular weights when dissolved in mercury; but we know that this is due to the heat of dilution, and that the real molecular weight is normal. Concentrated caustic potash or sulphuric acid solutions

show abnormally low molecular weights which cannot be accounted for by means of the dissociation theory or by means of "variations from the gas laws." These are solutions in which the heat of dilution is large. While it would be difficult to measure the heat of dilution for an infinitely dilute sodium chloride solution, there seems some prospect of reaching a conclusion by measuring the heats of vaporization. If the heat of vaporization of the salt solution does not differ from that of pure water, the molecular weight of sodium chloride is $\frac{1}{2}(23 + 35.5)$ and we have to account for the abnormal value. If the two heats of vaporization are different, the real and the apparent molecular weights will not be the same, and it may be that sodium chloride in water may be like sodium in mercury. The measurements necessary to decide this point must be made very accurately and they have been undertaken by Mr. Barnes, of McGill University. My own attitude in regard to the electrolytic dissociation theory will depend very largely on the result of these measurements.

Cornell University.

DISCUSSION.

MR. C. J. REED: There are some objections to the theory of electrolytic dissociation which seem not to have received proper consideration. No theory in science can be firmly established if it has points of weakness which will not bear scrutiny.

It seems to me one of the most fatal objection to the theory of electrolytic dissociation is one concerning energy. It is an objection to which I have already called your attention in Vol. III of our Transactions, in connection with the paper of Dr. L. A. Parsons, on "Ions and Electrons."

As this objection has not been answered, I consider it proper to repeat the objection at this meeting.

Dr. Roeber has referred to my objection without answering it. He says we are at liberty to make any assumptions for the purpose of constructing an analogical model and, citing the authority of Maxwell, he holds that analogy is a legitimate proof of the truth of a theory. This reminds me of the ancient method of

proving by analogy that there were seven planets in the solar system. "There are seven days in the week, and seven organs of sense, the eyes, nostrils, ears and mouth. Therefore, there must be seven planets or the whole system falls to the ground."

I am unfortunately so constituted mentally that I am unable to see in analogy a scientific method of discovering truth.

My premise in regard to the theory of electrolytic dissociation is that electrically-charged bodies are always potentially sources of electrical energy. That is, a system composed of two oppositely-charged bodies is always under stress and always tends to discharge itself. If the oppositely-charged bodies of an electrically charged system be connected by an external conductor of finite resistance, in such a way as to remove the charges, that is, discharge the particles or neutralizes them, there will always be a flow of current through the external conductor, due to this discharge. An electric current flowing through a conductor of finite resistance always communicates energy to the conductor. If the external conductor is itself charged or contains a source of counter-electromotive force capable of preventing the charged particles from producing á current through it, it also prevents the charged particles from giving up their charges or becoming neutralized. When, therefore, a system of oppositely-charged bodies gives up its charges to an external conductor they necessarily act as a source of electrical energy. If this premise is wrong its fallacy has not been shown. No instance has been cited, no illustration has been found, in which the discharge of electrically-charged particles is not, as stated above, a source of electrical energy.

Dr. Parsons, in his paper referred to above, says that he is not prepared to admit this premise. He does not deny it, however, nor offer a single instance in which it is not true.

Is it admitted that a system cannot produce a stress upon itself? Is it admitted that between oppositely charged particles there is always a condition of stress? If so, my premise is admitted; if not, the term "electrically charged," loses its meaning. If there is any member here prepared to refute this premise, I will allow him to interrupt me now for that purpose; if not, I shall proceed on the supposition that this premise is admitted, namely, that oppositely-charged particles necessarily constitute a source of energy.

The theory of electrolytic dissociation states that the oppositely-charged ions of an electrolyte always pass out of the electrolyte and cease to be ions by giving up their previously acquired opposite electric charges to the electrodes, which are always so connected electrically as to constitute a single conductor external to the electrolyte.

It must follow from this that electrochemical decomposition, or the electrodeposition and neutralization of ions at electrodes is a process in which the electrolyte or its charged ions always give up energy to an external conductor. This would be true whether the external conductor is itself a source of electromotive force or not.

The facts are entirely opposed to this conclusion. It is hardly necessary to say to this audience that in the electrodeposition of ions the electrolyte, instead of giving energy to the external circuit, always receives energy from the external circuit. I have not yet been able to find any case in which an ion gives up energy to the electrodes or external circuit in becoming an atom. If such were the case, metals would spontaneously reduce themselves from solutions on coming in contact with any conductor such as carbon or platinum.

It is at this point that mystery steps in, or is called upon to help out the theory of electrolytic dissociaton. It is admitted even by the advocates of the theory of electrolytic dissociation that "the chemical energy of the ions is smaller than the chemical energy of the atoms," to use the exact words of our esteemed member, Dr. F. Haber. How, then, can the electrolyte or its constituent charged ions give up electric charges, that is, give up electrical energy to a body external to the electrolyte in becoming discharged?

Dr. Parsons has fallen into the error of many other physicists in supposing that there is a difference other than one of degree in the potential energy of various elements in the metallic state. This error has come about by the erroneous supposition that certain metals have a negative solution pressure—that they have a spontaneous tendency to pass from the ionic state into the atomic or metallic state and to give up energy in so doing. But this is not true of any metal. The only difference between zinc and copper in this respect is that the energy given out by zinc in

changing from the atomic to the ionic state is greater than that given out by copper in the same process. The fact that copper ions are changed to atoms through the influence of metallic zinc is not due to any tendency of the copper to pass out of the ionic state, but is due to the greater tendency of zinc to pass into the ionic state and forcibly drive out the copper. The same statement applies to all metals with the possible exception of gold. The tendency of every metal to change from the atomic to the ionic state is measured directly by the formation heat of the compound in which it exists in the electrolyte.

Another serious objection to the theory of electrolytic dissociation is found in the electrolysis of fused electrolytes. The theory of electrolytic dissociation, as advanced by Arrhenius to account for the manner in which electrochemical separation takes place, entirely ignores the fact that there is a very large class of compounds in which electrochemical separation takes place, which are not solutions. In fused electrolytes electrolytic reactions take place in a manner similar to those of solutions, and they constitute a class of the same order of magnitude as the class of solutions. But it is impossible to apply the theory of electrolytic dissociation to fused electrolytes, and we are, therefore, compelled to have a separate theory for fused electrolytes if we retain the theory of electrolytic dissociation for solutions. According to this theory, electrochemical action or decomposition is merely the result of a directive influence upon the already separated constituents of the mass, while the actual separation occurs in the process of solution and before any electric current is applied. The formulæ governing the amount of this dissociation or separation have been mathematically worked out and connected with experimental determination of conductivity. The conductivity and other properties have been shown to bear certain relations to the amount of dissociation of a solute dissolved in a solvent. But how can we apply these formulæ or this theory to an electrolyte in which there is neither solvent nor solute, if dissociation is the result of mere solution of one body in another.

Some of the strongest arguments that have been used in favor of the theory were based upon the fact that certain compounds such as water and hydrochloric acid in a pure state, are nonconductors and when dissolved become electrolytes. Isolated

examples of this kind have been referred to as indisputable proof that solution is necessary for electrolytic conduction, and, therefore, that solution is a necessary prerequisite to electrolysis. But, as a matter of fact, there are as many insoluble electrolytes as there are compounds which are non-conductors in the pure state and conductors in solution.

There seems to me also to be a serious objection to the theory of solution pressure. If metals have a solution pressure which tends to cause their atoms to pass as ions into solution in a manner analogous to vapor pressure, as the theory supposes, it seems to me there is no escape from the conclusion that the quantity of a metal which will be dissolved in the solution, and the rate at which it will pass into the solution will be independent of the nature of the solution and depend only upon the solution pressure of the metal itself. In all acids free from zinc, for example, the solution pressure of the zinc ions in solution is zero. Consequently, zinc should dissolve with equal facility in all acids. The same should be true of all metals. It hardly seems necessary to point out that this is not true.

Another objection to the theory is that it does not account for the changes in concentration produced in electrolysis. An electrolyte of either uniform or non-uniform concentration, according to the theory of electrolytic dissociation, could undergo a change of concentration by the passage of electric current, only in the infinitesimal layer of electrolyte in immediate contact with the electrodes, and all changes in concentration produced elsewhere must be due entirely to other causes, chiefly to osmotic pressure. This is not sufficient to account for the actual changes in concentration which are observed, particularly the changes in concentration in portions of the electrolyte which are isolated from the electrodes, and in such cases as that described by me before this Society a year ago.

There are numerous other objections to the theory of electrolytic dissociation which have been ably set forth by Kahlenberg in the *Bulletin* of the University of Wisconsin, No. 47, February, 1901. I would also call particular attention to the luminous experiments of Kahlenberg on instantaneous chemical reactions between non-conducting solutions, which completely refute one of the strongest arguments in favor of the theory.

Referring again to the ingenious arguments of Dr. Roeber, I admit that he has constructed an analogical model, which, as far as analogies prove anything, may apply, as he says, to electrolytes of infinite dilution. But an electrolyte of infinite dilution is, according to the rules of mathematical proof, not an electrolyte, but pure water—a non-conductor. We have, therefore, in Dr. Roeber's argument, an excellent example of *reductio ad adsurdum*. I am not willing to admit the process of mathematical reasoning which enables us to conclude that whatever is true of anything at a zero value is also true at other values.

Mr. F. A. Lidbury: While the answer to a good deal of what Mr. Reed has said is not quite obvious at first sight, some of the arguments he has brought forward do not seem to bear very strongly on the question at issue. In the first place, does the dissociation theory really declare that for electrolytic conduction solution in another substance is necessary? Surely, no great stretch of the imagination is required to enable us to picture, in the case of fused salts mentioned by Mr. Reed, the current as being carried by the ions of the salt dissolved in the undecomposed fused salt; and in pure water, another case of "infinitely dilute solutions," measurements of the degree of dissociation into hydrogen ions and hydroxyl ions by several different methods agree exceedingly well.

Another point of which the bearing is not clear to me relates to the changes of concentration, some distance from the electrode, which attend the passage of the current. Such changes would naturally be expected as the result of changes of osmotic pressure at the electrodes, and, unless special precautions are taken, of convection currents due to local differences of temperature.

The other point to which I wish to refer relates to instantaneous reactions in non-conducting solutions. Dr. Roeber, as I understood him, made his position quite clear; he pointed out that though the hypothesis of electrolytic dissociation afforded a good explanation of instantaneous reactions in aqueous solutions, there was no logical need to suppose that the reverse must be the case; that is to say, that all cases of instantaneous reaction must be referred to electrolytic dissociation. That is quite another story.

MR. REED: Perhaps I gave a wrong impression. I meant to say that one of the strongest arguments that has been used in support of the theory is that of instantaneous chemical reactions in solutions, and I did not mean to say that Dr. Roeber took that view. I was only trying to refute that argument by referring to the experiments of Kahlenberg.

I think Mr. Lidbury did not understand what I said in regard to my experiment, and I will try to make it clear. I had a number of cells separated by porous partitions—three will serve for

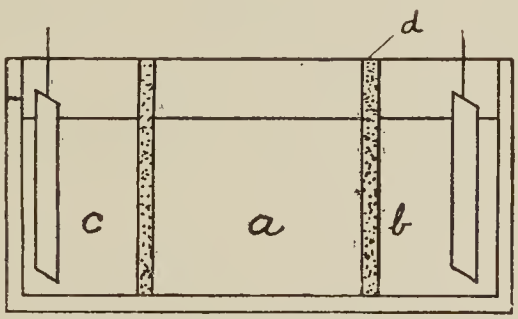


illustration. The central portion and that containing the electrode *c*, contained sulphuric acid of a given strength. In the compartment containing the electrode *b*, was a solution of copper sulphate. All three of the solutions were of exactly the same density at the beginning. The copper anode, *b*, was at a distance of 1 inch from the porous partition *d*, and a continuous stream of fresh electrolyte was passed through this anode compartment, so that it allowed no change of concentration in this compartment. When no current was flowing, only slight changes of concentration occurred in the central compartment and copper sulphate passed into the central compartment only very slowly, showing that the osmotic pressure of the copper salt had very little effect. As soon as the current was passed through, copper and H_2SO_4 passed rapidly into the central compartment, and the density, mass and volume of the liquid in that compartment all increased very rapidly, the density of the central electrolyte

becoming much greater than that of the electrolyte on either side—a result which could not have been produced by either osmotic pressure or electrical endosmose. Lamb has shown that electrical endosmose, or cataphoresis, can produce only hydrodynamic changes, and could not increase this density or change the chemical composition. That being the case, there is no other known cause which could produce that change in the concentration except the current; yet, according to the theory of electrolytic dissociation, there could be no change of concentration produced by the current except in the molecular layer adjacent to the electrode. That is the experiment that I referred to, and it does not appear to me that Mr. Lidbury's argument refutes it. For further details of that experiment, I would refer to Vol. II, page 235, Transactions of this Society.

Mr. Lidbury: I did not understand that you were referring to experiments in which a circulation of the electrolyte was kept up.

Dr. W. Lash Miller: It seems customary to interpose an objection after each vindication of the theory, so perhaps it is my turn. Some experiments carried out last winter with acetic acid gave results quite different from what the theory leads one to expect.

In the case of weak acids the theory of electrolytic dissociation is very specific; taking acetic acid for example, freezing point and conductivity determinations—and particularly the fact that the latter obey Ostwald's dilution law—lead to the conclusion that the ions are hydrogen, and the acet-ions $C_2H_3O_2$. But if we assume that these are the ions, we ought to be able to predict the transport, or migration of the acetic acid when a current of electricity passes through an acetic acid solution.

In a cell containing dilute acetic acid, divided into a cathode compartment and an anode compartment, when the current passes hydrogen ions should move into the cathode compartment, and acet-ions out of it; and since the hydrogen ion moves six times as quickly as the acet ion, six hydrogen ions should enter the cathode compartment and one acet ion leave it, while seven times 96,540 coulombs pass through the solution. (In the figure the

acetic acid is represented in the usual way, by a row of hydrogen ions, H, and a row of acet-ions A).

Before HHHHHHHHH|HHHHHHHHH
AAAAAAAAA|AAAAAAAAA

After HH|HHHHHHHHHHHHHHH
AAAAAAAAA|AAAAAAA

The experiment can be so arranged that the hydrogen which enters the cathode compartment leaves at the cathode in the form of hydrogen gas, and the same thing happens to the hydrogen which was paired with the acet-ion which left the compartment, that the net result of the passage of $7 \times 96{,}540$ coulombs should be that one molecule (60 grams) of acetic acid leaves the cathode compartment. I won't enlarge upon this, because it is an ordinary deduction from the theory.

So far as I am aware, no measurement of the transport in solutions of weak acids have, as yet, been published. In experiments carried out last winter under my direction by Mr. McBain, he found that the loss of acetic acid was two or three times as great as the theory predicts. If we adhere to the ions H and A, we must conclude that the hydrogen ion moves only about twice as fast as the acet-ion, but this assumption is not in accordance with the theory's explanation of the conductivity measurements. If, on the other hand, we assume different ions, say, H and HA_2 (something after the manner in which Hittorff explained his experiments with cadmium iodide), we again conflict with the conductivity measurements. So, that, as I am not anxious to overthrow the dissociation theory—it is very handy in giving lectures (Laughter and Applause)—I have looked for some other explanation, and this has occurred to me, that perhaps the solution of acetic acid might be regarded as containing the ions H and A in a solvent composed of undissociated acetic acid and water, just as in a mixture of alcohol and brine, the ions might be Na and Cl in a solvent composed of alcohol and water. Can any member of the Society let me know whether in the latter case the alcohol moves out of the cathode compartment, into the anode compartment, or vice versa?

To assume motion of the undissociated acetic acid seems the

only explanation available, if one takes for granted that the facts are as stated, and I have tried to assure myself that they are, although as the experiments are not yet finished I cannot give details as to the exact amount of acid that leaves the cathode per coulomb under different conditions of temperature, concentration, etc. The experiments, so far, have been carried out with tenth-normal and half-normal acetic acid at 30°.

Dr. H. S. Carhart: Dr. Bancroft has been very fair in presenting both sides of the electrolytical dissociation theory, that is, in presenting some of the facts in favor of the theory, as well as some of the objections that can be urged against it. I admired very much his fairness in this particular. The electrolytic dissociation theory so far has been a very useful working hypothesis. No one can deny that. It has led to the discovery of a large number of facts and to the explanation of a great many others, which, to say the least, have not been so readily accounted for heretofore, and, until it has been disproved, it ought to be retained as a working hypothesis. Still, we cannot ignore the objections that are brought against it, and many of these objections are, to my mind, very serious. In the first place, the name that has been applied to it, at least the adjective electrolytic that is associated with the dissociation theory, does not seem to be entirely appropriate. I suppose it is to distinguish it from thermal dissociation, but if the dissociation takes place on solution, why is it called electrolytic, when electrolysis has nothing to do with it? That is a minor point, of course.

The question of the source of the energy concerned in the dissociation seems to me to be one of the most serious difficulties with the theory. The difficulty, so far as I have observed, is always either ignored or the writer begs the question, assuming that there is always chemical energy in the solution that has not been used up, and that some of this performs the operation of the dissociation of the salts, but that is begging the question and is not a fair answer. Then, again, when the theory is considered from a quantitative point of view I have been very much struck with the fact that the proofs do not stand quantitatively as well as we might desire. The relation is often a very rough one. While the theory that the ions act like a gas in producing osmotic pressure seems to be in many cases, at least, extremely well sup-

ported; in other respects, the quantitative proof of the theory is very rough, indeed. It is altogether too rough, I am sure, to suit a physicist. The theory, perhaps, is going through a historical development or evolution quite similar to what has taken place in the past in astronomy. The old theory of cycles and epicycles undoubtedly served a very useful purpose for many years, but as more facts were accumulated and astronomy became more quantitative, it was found that the theory became entirely too complicated, and epicycles, as you know, gave way to the motion of the planets in ellipses, and we had the new astronomical theories. Is it not entirely probable that we shall not have the dissociated theory displaced by a totally different one, but rather some profound modification of the dissociation theory, which will account for a very much larger number of facts, quite analogous to the displacement of the old theories in astronomy by the modern ones which now prevail?

For myself, I take the position that the dissociation theory is a very useful working hypothesis, not to be despised by any means, but that it has perhaps been worked a little too hard when we consider many of the facts which may be arrayed against it.

Mr. James Locke: May I ask Professor Bancroft exactly what he meant by his statement that our interest in the analogy between dissolved substances and gases has led to neglecting the analogy between dissolved substances and liquids? I want to find out exactly what he meant by that.

Dr. W. D. Bancroft: The thing that I meant was, that it has led us to postulate that you can have a decrease of solubility only when you have an ion in common, and that all other dissolved substances must behave like gases and can, therefore, not have any effect on the solubility. You will find a statement by Nernst that the action of alcohol in dilute solutions on the solubility of salts is practically negligible and not to be considered as anything like so important as the action of another salt in common ion. That statement is not in accordance with facts, and I could go on and duplicate statements of that same general nature indefinitely. You have it coming up again in the distribution law, where it is postulated explicitly, that the addition of the third substance does not make the other two substances more miscible one with the other; whereas that happens in all

cases. Sometimes the change of solubility is very slight, but if you add alcohol to benzene and water, you finally get one liquid, if you add enough alcohol.

MR. LOCKE: The reason I asked was because probably the proof which has gradually been coming from inorganic chemistry has given the electrolytic theory a greater set back than anything else. The chief advantage which the electrolytic theory has offered to the inorganic chemist and to the analytical chemist has been in the possibility of applying the law of mass action. We have heard a great deal in the last year or two about concentrated solutions acting as entirely different liquids; and it seems to me that all that variation or discrepancy between the calculated values of the solubility products and the actual facts is due purely and simply to the fact that we do not know anything about the law of dilution. All the instances of discrepancy that have arisen have been found where bodies do not obey the law of dilution, and were due solely to the fact that the law of dilution has never been investigated. There is no reason in the world, it seems to me, from what analogy we can find in organic chemistry, to assume that there is the slightest difference as far as the dilution is concerned, between the effect of water on a salt and the effect of a solution of another salt.

PRES. RICHARDS: Professor Carhart has brought up the subject of the energy, which is concerned in the act of electrolytic dissociation, and since my paper is largely concerned with that, I will read my contribution to that part of the discussion.

(The paper of Dr. Jos. W. Richards, on "The Thermochemistry of the Theory of Electrolytic Dissociation," was here read, as printed on page 137 of these Transactions.)

PRES. RICHARDS: I will call upon Mr. Reed for his paper on the Berthelot law, as it has more or less connection with the subject of the neutralization of acids.

MR. REED: As this paper has already been presented in the form of advance sheets, and is accessible to all the members who care to read it, it seems to me we should take what time there is to finish this discussion. I think there are quite a number of gentlemen here, from whom we should all like to hear on this subject. I will ask, therefore, that the paper be read by its title.

PRES. RICHARDS: The paper having been already postponed

and Mr. Reed asking that it be read by title, further discussion is in order.

The paper of C. J. Reed, entitled "Berthelot's Law Relative to the Electromotive Forces of Cells Based on the Reciprocal Action of Saline Solutions and Soluble Electrolytes," as printed on page 151 of these Transactions, is accordingly read by title.

Dr. W. S. Weedon: This state of combination which President Richards has spoken of, if it exists, must be different from what we generally concede combination to mean. One common illustration will suffice to show the rather independent state of ions in salt solutions. Dilute solutions of sodium chloride and potassium iodide when mixed (molecular proportions being used), behave exactly as does a mixture of potassium chloride and sodium iodide. On the other hand, a mixture of ethyl bromide and methyl iodide does not resemble one of methyl bromide and ethyl iodide, as here there is no dissociation.

Mr. Cowles: It seems to me that in considering the question of the energy, we should not think alone of the molecules that are dissociated into ions, and lose sight of the solvent. We deal with the stored-up energy in the whole mass of the solution. One can imagine the molecules of the solvent and the dissociated ions as being connected together by invisible springs, as it were. The molecules that are dissociated throw stresses and cause strains in the molecules of the solvent. The energy that causes the dissociation, may thus be stored up in the stressed molecules of the solvent, thus not altering the total energy of the system, the total energy remaining the same, though certain of the solvent molecules be dissociated into ions. Taking this view of it, Prof. Richards explanation to the effect that there is no actual consumption of energy in the breaking up of the molecules into ions, would be explained. We must look at all the molecules of the solvent and the solute collectively, and not alone think of those molecules that are dissociated into ions with an absorption of energy in virtue of that one action.

Mr. Reed: There is one experiment I would like to call attention to and ask for an explanation. I observed one day that when nitric acid is mixed with hydrobromic acid there is apparently no chemical change whatever. The mixture is a conductor. On slightly heating it a chemical change takes place, with the precipi-

tation of a large quantity of the red liquid bromine. Now, if dissociation took place when the two were mixed together with the production of ions, and if those ions are what produced the chemical change, why were they not produced as soon as they were mixed together? What was the difference between the ions after heating and before? Certainly a difference in the chemical constitution.

According to Mr. Cowles, energy is taken from the water in dissociation and stored in the ions. We might suppose this to be the case if the ions never passed out of the electrolyte and never gave up their charges to an external body. But when they do that it makes the water an inexhaustible source of electric charges, or of energy.

Pres. Richards: My view of the point raised by Doctor Weedon is that when you mix two solutions together it makes no difference whether you start, for instance, with potassium chloride and sodium bromide, or potassium-bromide and sodium chloride: that when they are mixed together the resulting solution is of the same—has the same properties whichever two salts you start from, and the point which he brings up of the dissociation of the compound has been well answered by Mr. Cowles. Mr. Cowles' expression amounts to saying that there is practically no energy lost or gained in the act of ionization, and, therefore, the compound from the energy standpoint is practically as much a compound after ionization as it was before.

Dr. Carhart: Then what is the change, is the question, constituting ionization?

Pres. Richards: I wish I knew. (Laughter).

Mr. Cowles: A change of relative position of the atoms, that involves possibly the dissociation of the molecules, upon the removal of energy from the mass of the solution. The energy that may be stored up in one pair of atoms when they are linked together, has a certain intrinsic value. When you part them, one would naturally think that you add to that value, but that energy that is thus added, may lessen the store of potential energy in the molecules of the solvent. The total energy of the system is unchanged. If it costs energy from an electric current to sweep some of the ions out of the solution, then a chance is created for more dissolved molecules to dissociate into ions, but this latter

action is one that takes place without alteration of the energy of the system.

Prof. H. M. Goodwin: My attitude towards the dissociation theory at the present time has already been very well expressed in the remarks made by Professor Carhart. I feel that it has been, and still is, too useful a working hypothesis—an hypothesis which has given at least a plausible explanation of the relations between too many obscurely-related physical and chemical phenomena—to be lightly set aside because of the objections which have, as yet, been raised against it. Difficulties, of which the failure of the dilution law for solutions of inorganic compounds is perhaps one of the most serious, have long been recognized, but whether such exceptions and others more recently established will ultimately necessitate the abandonment of the hypothesis or only its modification, is a question which only the future can decide.

The question of the energy transformation involved in the dissociation of a substance in solution seems to me best explained on the assumption that a displacement of the equilibrium of the forces holding the atoms together in the molecule takes place in virtue of the presence of the surrounding medium of high dielectric constant, whereby the atoms gradually separate by an amount depending upon the dilution, until they finally act as free ions. The equivalent of the work thus performed reappears as heat when the ions reunite, as, *e. g.*, in the reunion of hydrogen and hydroxyl ions in the neutralization of an acid or a base. This assumption seems to be supported by the experimental evidence confirming the Nernst-Thomson law and also by certain spectrophotometric studies on solutions of copper salts which have been carried out in our laboratory. It has been shown that the effect of the solvent (water) on copper sulphate is such that the characteristic selective absorption of the copper atom manifests itself long before the atom becomes so separated from the molecule as to act as a conductor of electricity, that is, as an ion. At first sight the explanation just offered by Professor Richards for the origin of the heat of neutralization seems to me no simpler than the above: the agreement between his calculated and observed values is, however, interesting and striking.

Pres. Richards: The point which I raised was that since a

dilute solution containing H and OH ions exerts osmotic pressure analogous to its condition in a state of gas, and since, after the neutralization, you certainly have liquid water, there has been a transition from a state analogous to the gaseous state, to water in the liquid state, and the heat of condensation from gaseous to a liquid state comes in. The latter coincides fairly well with the observed heat of neutralization.

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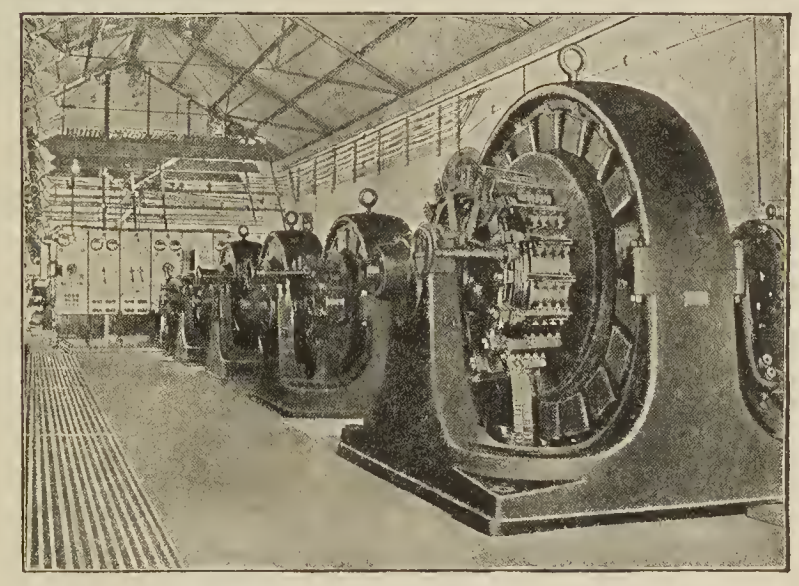

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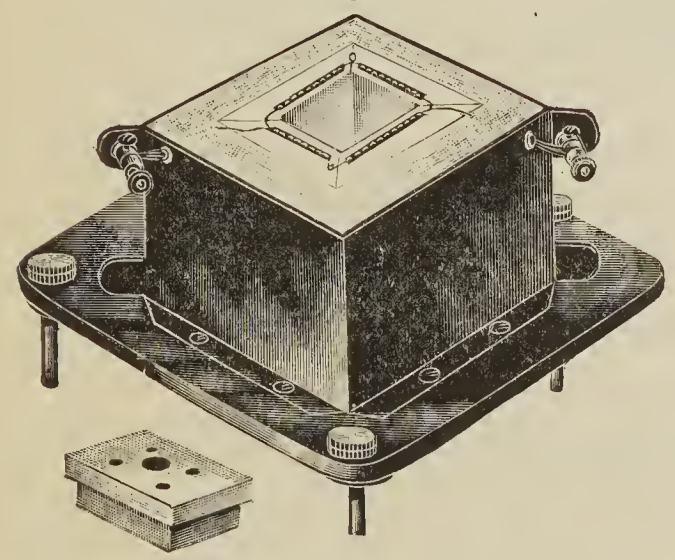

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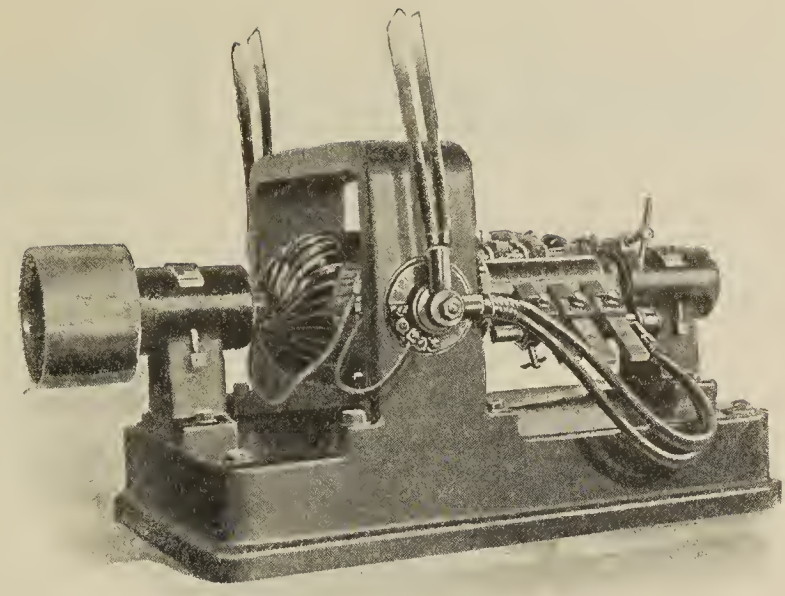

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